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Chapter 2 - Nanoscale Systems

Syllabus: Length scales in physics, Nanostructures: 1D, 2D and 3D nanostructures (nanodots, thin films, nanowires, nanorods), Band structures and density of states of materials at nanoscales, Size effects at nanosystems, Quantum confinement: Applications of *Schrödinger* equation, Infinite potential well, potential step, potential box, quantum confinement of carriers in 3D, 2D and 1D nanostructures and its consequences.

1 Introduction

Nanotechnology is the most widely used term in the modern scientific and technological literature. The concept of nanotechnology appeared for the first time in the famous talk "THERE IS PLENTY OF ROOM AT THE BOTTOM" delivered by the great physicist Richard Feynman at the American Physical Society meeting at Caltech on December 29, 1959. In his lecture, Feynman described how individual atoms and molecules could be manipulated to prepare low dimensional materials and to develop nano-machines for technological applications. He stressed further that scaling issues would arise from changing the magnitude of various physical phenomena; gravity would become less important but the surface effects would become increasingly more significant. The term nanotechnology was originally defined by Norio Taniguchi in 1974 in the following way: *"Nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or by one molecule"*. Since then nanotechnology and nanoscience got an upsurge and many new scientific developments came into reality. Two such major developments are: the advances in computing power and material modeling and significant improvements in characterization of nanomaterials with the use of scanning tunneling microscope (STM) and the atomic force microscope (AFM). These lead new directions to the study of nanomaterials,

The field of nanotechnology is now growing very rapidly. It is the collaboration of the physics, chemistry, biology, computer and material sciences integrated with nanoscale engineering. Hence it is truly an interdisciplinary subject. In nanotechnology, scientists focus on the study of phenomena and manipulation of particles, things and devices at atomic, molecular, and macromolecular scales where properties differ significantly from those at macroscopic (larger) scales. The difference in microscopic and macroscopic properties mainly arises due to the high surface to volume ratio (aspect ratio) and the appearance of quantum effects at the microscopic (nano) scales. Nanotechnology deals with design, characterization, production, and applications of nanomaterial-based devices in industry and technology. Nanomaterials are used in almost all commercial products including medical equipment, textiles, fuel additives, cosmetics, plastics and more. In such applications, shape and size of the materials at the nanoscale play dominant role. These materials are currently produced in metric tons per year and are expected to increase exponentially as new advances emerge out. Researchers are relentlessly pursuing from different routes to create nanomaterials and to understand their physical and chemical relationship between composition, size, and morphology to incorporate nanomaterials into everyday life.

✓ Nanomaterials exhibit various physical properties such as electrical, optical and magnetic. Magnetic nanoparticles are used in a range of applications like imaging, bioprocessing, refrigeration as well as high storage density magnetic memory media. The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighboring atoms leading to differing magnetic properties. Bulk gold and platinum are non magnetic but at the nano size they act as magnetic particles. Au nanoparticles become ferromagnetic when they are capped with the appropriate molecules such as thiol. Giant magnetoresistance (GMR) is a phenomenon observed in nanoscale multilayers consisting of strong ferromagnet (Fe, Co, Ni) and a weaker magnetic or non magnetic buffer (Cr, Cu). It is usually employed in data storage and sensing.

Dimension at the nanoscale plays a significant role in the appearance of physical properties of nanomaterials. For example, the reduced dimensionality ~~has the most profound effect~~ on the energies of highest occupied molecular orbital (HOMO) [valence band] and the lowest unoccupied molecular orbital (LUMO) [conduction band]. The optical emission and adsorption occurs when the transition of the electrons occur between these two states. Semiconductors and many metals show large changes in optical properties such as color, as a function of particle size. Colloidal suspenses of gold nano particles have a deep red color which becomes progressively more yellow as the particle size increases. Gold spheres of diameter 10-20 nm exhibit red color. But the gold spheres of diameter 2-5 nm exhibit yellow color while that of diameter $>$ 20 nm exhibit purple color. Similarly, silver particles of 40 nm size exhibit blue color while such silver particles of 100nm size exhibit yellow color. Prism shaped silver particles show red color. Reduced dimensionality also affects other optical properties such as photocatalysis, photoconductivity, photoemission and electroluminescence. ✓

The reduced dimensionality changes the electronic structure of nanomaterials. Such changes in electronic properties occur mainly due to the increasing influence of the wave-like property of the electrons (quantum mechanical effects) and the scarcity of scattering centers. As the size of the system becomes comparable with the de Broglie wavelength ($\lambda_{dB} = \frac{h}{p}$, h is Planck's constant and p is the momentum) of the electrons, the discrete nature of the energy states becomes obvious, although a fully discrete energy spectrum is only observed in systems which are confined in all three dimensions. In certain cases, conducting materials become insulators below a critical length scale, as the energy bands cease to overlap. Owing to their intrinsic wave-like nature, electrons can tunnel quantum mechanically between two closely adjacent nanostructures.

If a voltage is applied between two nanostructures which aligns the discrete energy levels in the density of states, resonant tunneling occurs, which abruptly increases the tunneling current. Conduction in highly confined structures, such as quantum dots, is very sensitive to the presence of other charge carriers and the charge state of the dot. Coulomb blockade effects result in conduction processes involving single electrons. In such a single electron transport process, only a small amount of energy is required for conduction and as a result, devices using single electron can be operated as a switch, transistor or memory element with very small amount of power. These phenomena can be utilized to produce radically different types of components for electronic, optoelectronic and information processing applications, such as resonant tunneling transistors and single-electron transistors.

In this chapter, band structure, density of states and quantum confinements of various types of nanostructures (1D, 2D and 3D) such as nanodots, nanowires, nanorods and thin films are discussed in details.

2 Length scales in physics

The prefix of nanoscience and nanotechnology is derived from the unit of length, the nanometer. In their broadest definitions, the terms "nanoscience and nanotechnology" refer to the science and technology that is based on length scales from one nanometer up to 100 nanometers or so and is able to assemble, manipulate, observe and control matter in this nanoscale range. One nanometer is a billionth of a meter or one thousandth of a micrometer, sometimes called a micron, which in turn is one thousandth of a millimeter. It is abbreviated to 1 nm. These numbers can be put into context by observing that a medium-size atom has a size of a fraction of a nm, a small molecule is perhaps 1 nm, and a biological macromolecule such as a protein is about 10 nm. A bacterial cell might be up to a few thousand nanometers in size. The smallest line width in a modern integrated circuit, such as would be found in a fast home computer, is few hundred nm.

Physicists try to understand and figure out how the universe works. This requires to understand the processes which are larger than the galaxies and even those ones which are smaller than atoms. To describe exactly how big or how small things are, we use units of measurements. If we want to know how big atoms and molecules are, we should start by understanding Bohr radius. The Bohr radius as obtained by optimizing $E_{tot} = \frac{\hbar^2}{2mr^2} - \frac{e^2}{r}$ $(r = \frac{\hbar^2}{m e^2})$ is the approximate size of a hydrogen atom in its ground state. It is only approximate, because the electron in a hydrogen atom is a fuzzy probability cloud, not a pellet whizzing around in a circular orbit. The Bohr radius depends on the electron mass, the electron charge and Planck's constant. The Bohr radius is inversely proportional to the mass of the electron. This is an example of a general phenomenon in particle physics: a mass scale (electron mass) sets an inverse length scale (Bohr radius).

✓The Compton wavelength of a particle is the length at which relativistic quantum field theory becomes crucial for its accurate description. If we try to localize an electron to within less than its Compton wavelength makes its momentum so uncertain that it can have an energy large enough to make an extra electron-positron pair. This is the length scale at which quantum field theory, which describes particle creation, becomes really important for describing electrons. The Compton wavelength of the electron is the characteristic length scale of quantum electrodynamics (QED). The Compton wavelength is given by $L_{Compton} = \dfrac{\hbar}{mc}$. This is about 4×10^{-13} meters. In fact, this is the reduced Compton wavelength. The ratio of the Bohr radius to the Compton wavelength is given by $\frac{\frac{\hbar^2}{m_e e^2}}{\frac{\hbar}{mc}} = \frac{\hbar c}{e^2}$. It is roughly about 137. This is a famous number, one over the fine structure constant. Hence it is good to keep in mind for a gut-level understanding of microphysics that the effects of quantum field theory start really significant for electrons on a distance scale of $\frac{1}{137}$ the size of the hydrogen atom. This is the reason people were able to notice these field-theoretic effects and develop QED not too long after they came up with a quantum-mechanical description of the hydrogen atom. ✓

In quantum mechanics, the length scale of a given phenomenon is related to the de Broglie wavelength λ_{dB}. In relativistic mechanics time and length scales are related by the speed of light c. In relativistic quantum mechanics or relativistic quantum field theory, length scales are related to momentum, time and energy scales through Planck's constant h and the speed of light c. Often in high energy physics, natural units are used where length, time, energy and momentum scales are described in the same units usually with units of energy such as GeV. It should be mentioned that $1\ GeV = 10^9\ eV$.

Length scales are usually the operative scale (or at least one of the scales) in dimensional analysis. For instance, in scattering theory, the most common quantity to calculate is a cross section which has units of length squared and is measured in barns ($10^{-24}\ cm^2$). The cross section of a given process is usually the square of the length scale.

The atomic length scale is $l_a \sim 10^{-10}$ meters and is given by the size of hydrogen atom (i.e., the Bohr radius (approximately 0.53$\mathring{A}$)) which is set by the electron's Compton wavelength times the inverse of fine-structure constant: $l_a \sim \frac{1}{\alpha m_e}$. The length scale for the strong interactions (or the one derived from QCD through dimensional transmutation) is around $l_s \sim 10^{-15}$ meters (or in natural units 1000 MeV or 1 GeV), and the "radii" of strongly interacting particles (such as the proton) are roughly comparable. This length scale is determined by the range of the Yukawa potential. The lifetimes of strongly interacting particles, such as the ρ meson, are given by this length scale divided by the speed of light: 10^{-23} seconds. The masses of strongly interacting particles are several times the associated energy scale (500 MeV to 3000 MeV).

The electroweak length scale is shorter, roughly $l_w \sim 10^{-18}$ meters and is set by the rest mass of the weak vector bosons which is roughly 100 GeV. This length scale would be the distance where a Yukawa force is mediated by the weak vector bosons. The magnitude of weak length scale was initially inferred by the Fermi constant measured by neutron and muon decay.

2.1 Planck's scales in physics

The Planck's constant h has magnitude of $6.626 \times 10^{-34}\ Js$. This constant plays two roles. In its traditional form, h is the proportionality constant that relates frequency and energy for electromagnetic radiation. It is sometimes called the quantum of action. In its reduced form, $\hbar \left(= \frac{h}{2\pi}\right)$ is the quantum of angular momentum. Many of the researchers consider the second form to be more fundamental of the two but it did not appear until 1930. On the other hand, the two constants, the speed of light c and universal gravitational constant G had a long and distinguished history, Planck's constant had never been seen before. His revolutionary paper on blackbody radiation was not published until 1901 - two years after he proposed the system of natural length unit.

The procedure for generating the Planck length (Planck's length scale) is to combine four fundamental constants: the speed of light $c(= 299,792,458\ ms^{-1})$, universal gravitational constant $G(= 6.67428 \times 10^{-11}\ Nm^2kg^{-2})$, Boltzmann constant $K_B(= 1.3806504 \times 10^{-23}\ JK^{-1})$ and Planck's constant $h(= 6.626 \times 10^{-34}\ Js)$ in a way that gives an answer with the right unit of length. This is the length scale at which quantum gravity should become important. On the scale of the Planck length, it is possible that the structure of space-time becomes quite different from the four-dimensional manifold. Space-time itself becomes a foam (according to Wheeler) or a bucket of dust (according to Wheeler) or a bubbling sea of virtual black holes (according to Hawking) or a weave of knots or tangles (according to Ashtekar, Rovelli, and Smolin). To be more precise, the Planck length is the length scale at which quantum mechanics, gravity and relativity all interact very strongly. By combining the universal constants, this Planck length is obtained in the following way:

$$\checkmark \quad l_P = \sqrt{\frac{\hbar\, G}{c^3}} = \sqrt{\frac{(1.055 \times 10^{-34}) \times (6.67428 \times 10^{-11})}{(299,792,458)^3}} = 1.616 \times 10^{-35}\ m. \quad \checkmark \tag{1}$$

The Planck length (Planck scale) is much shorter yet - about $l_P \sim 10^{-35}$ meters ($10^{19} GeV^{-1}$ in natural units), and is derived from Newton's gravitational constant which has units of length squared. This Planck length is small beyond comprehension. The next biggest material thing is a proton, the diameter of which is of the order of $10^{-15}\ m$. This diameter is a full 20 orders of magnitude bigger than the Planck length scale. Think of something that is about $10^5\ m$ across (100 km). The big island of Hawaii comes to mind. If a proton was blown up to the size of the island of Hawaii, the Planck length would be as big as the original proton.

The Mesoscopic scale is the length at which quantum mechanical behaviors in liquids or solids can be described by macroscopic concepts. Here in this chapter we will concentrate only on the nanoscale structures of materials.

3 Nanostructures

Nanostructured materials are called nanomaterials and are being studied extensively due to their great potentials in technology. These nanomaterials have been observed to exist in various historical activities of human society. Some of the evidences are the discovery of multiwalled carbon nanotubes (MWCNT) within swords fabricated with Damascus steel in around AD 500, their presence within stained glass paints, and within the smoke of early human made fires. Though nanomaterials have been used in practical applications far back in human history, it is only in recent times that it has been possible to synthesize and characterize these structures in a controlled manner. Some of the well-known synthesis are: Michael Faraday synthesized gold colloidal solutions in 1857, Nario Taniguchi developed nanometer precision production technologies in the late 1960s, and IBM introduced the scanning tunneling microscope (STM) in 1981. The discoveries in nanomaterials have evolved along with their production and characterization. For example, in recent times the following new allotropes of carbon have been discovered: fullerenes in 1985, carbon nanotubes in 1991, and graphene in 2003. Many new experimental techniques have been developed and are being easily accessible to synthesize and characterize topology, mechanical properties, porosity, and composition of nanoscale systems. Materials have a wide range of spatial extensions. Some examples of the materials available in nature with their spatial extensions are shown in Figure 1.

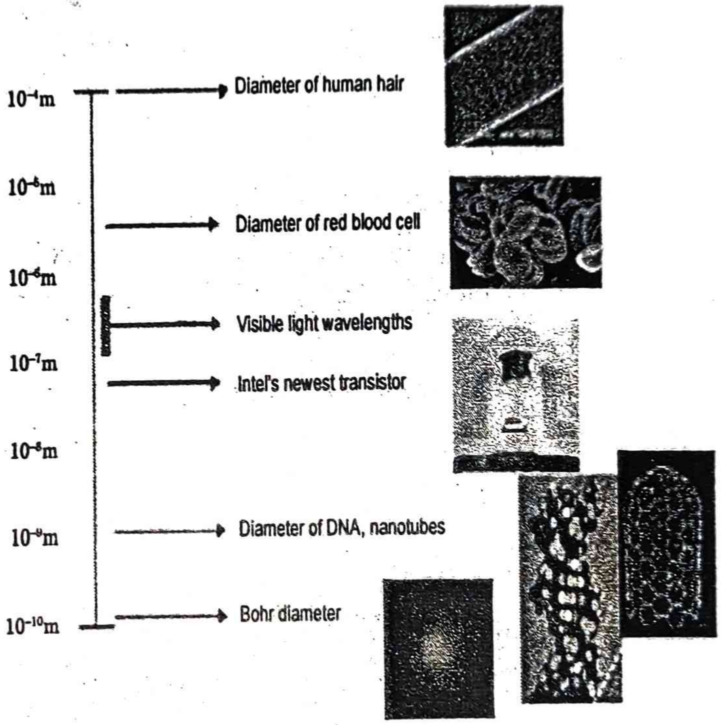

Figure 1: Spatial extension in meter of some naturally occurring materials.

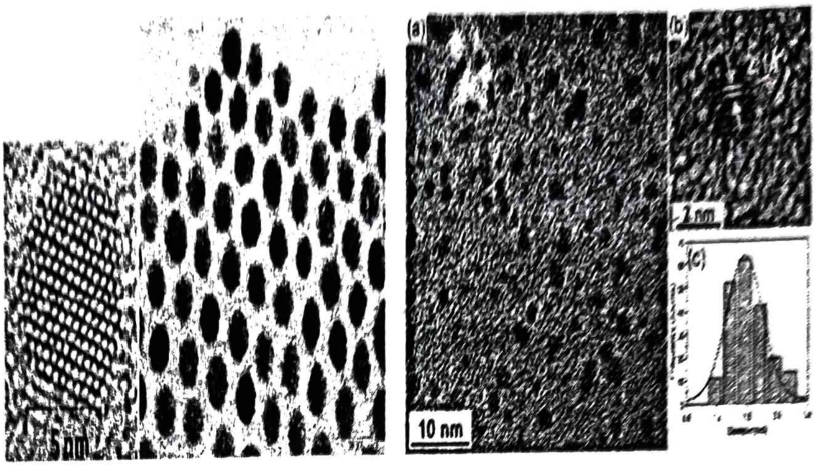

Figure 2: CdSe core quantum dots with CdS and ZnSe (left) and carbon quantum dots (right). Look at the scale and size distribution. (Courtesy: Internet)

Among various experimental techniques used in nanotechnology, micro-Raman and Fourier transform infrared spectroscopy (FTIR) are two very important instruments. Micro-Raman spectroscopy is commonly used to detect specific molecular bonds. For this technique, the sample to be analyzed is generally illuminated by laser light with frequency within the visible, infrared, or ultraviolet ranges. Reflected light is focused through a monochromator filtering out wavelengths close to the laser wavelength to allow the detection of other scattered wavelengths. A very small percentage of scattered photons are scattered by excitation and having a frequency different (usually lower) from the frequency of the incident photons. As this frequency is specific to the chemical bond under investigation, it allows identification of the species. FTIR is similar to Raman spectroscopy in that the vibration of molecular bond is used for identification of chemical species. In FTIR, the resonant frequency of bond vibration after exposure to infrared radiation is detected as an identifier for the species under examination. Most commercial instruments automatically suggest the type and quantity of species present by comparing the spectra to large databases of reference spectra.

Nanomaterials are evident in the natural environment as in air-borne particles which cause water to condense into rain, as plankton in the sea, and in metal and mineral ores as intermetallic particles. These materials are also present in biological systems in various forms such as proteins, DNA, and viruses. At the nanometer size ranges, nanomaterials show unique properties attributed to the increased surface area, altered electronic states, or to incomplete or novel lattice structures being formed. Density functional theory (DFT) is now being used to predict arrangement of atoms and to evaluate what type of properties might arise therein. Further DFT can predict magnetic, optical, biological, and mechanical properties of nanomaterials and can be utilized as a sophisticated tool to handle nanomaterials.

Nanotechnology has and will have a large impact on the technological development in the future. These developments include engineering applications ranging from enhanced corrosion resistance and antimicrobial surfaces in implants, enhanced strength of structural materials, more absorbable pharmaceuticals as nanolubricants, for easier electron generation and transfer in electronic and electrical systems, in novel materials for communication, and data storage, and in analytical and diagnostic applications. There are some challenges remaining for nanostructure material research. These include the ability to fabricate usefully large quantities of the nanostructure materials, obtaining a uniform distribution of nanostructures within a colloid or as a surface coating, generating a uniform allotrope type and size range of structures, and the development of lower cost and faster characterization techniques. As an example, a major challenge of fabricating carbon nanotube (CNT), reduced graphene oxide (rGO) or graphene reinforced metals as structural materials lies in the task of achieving a homogeneous dispersion of the carbonaceous reinforcing material within the metal matrix without destroying the original microstructure of reinforcing materials or introducing additional impurities to the composite during production.

The nanostructure materials can broadly be classified into four general categories as given below:

1. Zero dimensional nanostructures.
2. One dimensional nanostructures.
3. Two dimensional nanostructures.
4. Three dimensional nanostructures.

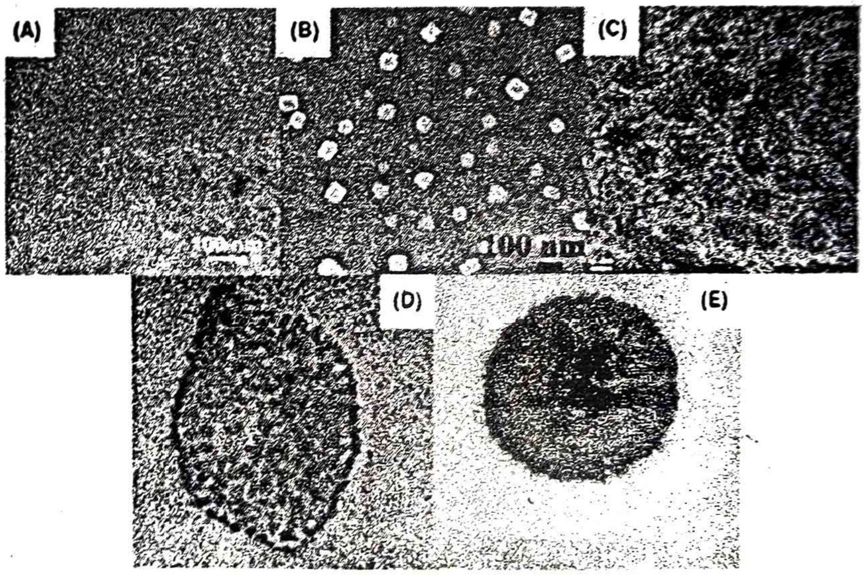

Figure 3: Typical SEM and TEM images of various zero dimensional nanostructures: (A) quantum dots, (B) nanoparticles arrays, (C) core-shell nanoparticles, (D) hollow cubes, and (E) nanospheres.

3.1 Zero dimensional nanostructures:

Dimensionality is a major factor that discriminates various types of nanostructures. We know that the word 'nano' is assigned to indicate the number 10^{-9}, i.e., one billionth of any unit. In case of zero dimensional (0D) nanomaterials, all dimensions are measured within the nanoscale. No dimensions are larger than 100 nm. 0D nanomaterials can

1. be amorphous or crystalline.
2. be single crystalline or polycrystalline.
3. be composed of single or multi-chemical elements.
4. exhibit various shapes and forms.
5. exist individually or incorporated in a matrix.
6. metallic, ceramic, or polymeric. ✓

In the past 10 years, significant progress has been made in the field of zero dimensional nanostructure materials. A rich variety of physical and chemical methods have been developed for fabricating zero dimensional nanostructure materials with well controlled dimensions. Recently, zero order nanostructure materials such as uniform particle arrays (quantum dots), heterogeneous particle arrays, core- shell quantum dots, onions, hollow spheres and nanolenses have been synthesized by several research groups. Typical images of quantum dots are shown in Figure 2. The image in the left shows quantum dots of $CdSe$ core with CdS and $ZnSe$ whereas that in the right shows quantum dots of carbon. The scale in the figure indicates the spatial extension of the nanoobjects. Some zero dimensional nanostructures are also shown in Figure 3.

✓3.2 One dimensional nanostructures

In the last decade one dimensional nanostructure materials have stimulated an increasing interest due to their importance in research and developments. After the pioneering discovery of carbon nanotubes by Iijima, the field of one dimensional nanomaterials has reached to a level of significant development. It is generally believed that these materials serve as ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of functional properties. One dimensional nanomaterials are being used in a wide range of potential applications in electronic, optoelectronic and light emitting diodes (LEDs) with nanoscale dimensions and have a profound impact in nanodevices, nanocomposites, alternative energy resources and national security. 1D nanomaterials can be

1. amorphous or crystalline.
2. single crystalline or polycrystalline.
3. chemically pure or impure.
4. standalone material or embedded in within another medium.

5. metallic, ceramic, or polymeric.

Examples of one-dimensional (1D) nanostructure materials include nanowires, nanorods, nanotubes, nanoribbons and quantum wires. Some of these one dimensional structures are shown in Figure 4. These materials have been regarded as the most promising building blocks for nanoscale electronic and optoelectronic devices. Worldwide efforts in both the theory and the experimental investigation of growth, characterization and applications of 1D nanostructures have resulted in a mature and multidisciplinary field. In this book, a wealth of state-of-the-art information offers the opportunity to uncover the underlying science from diverse perspectives.

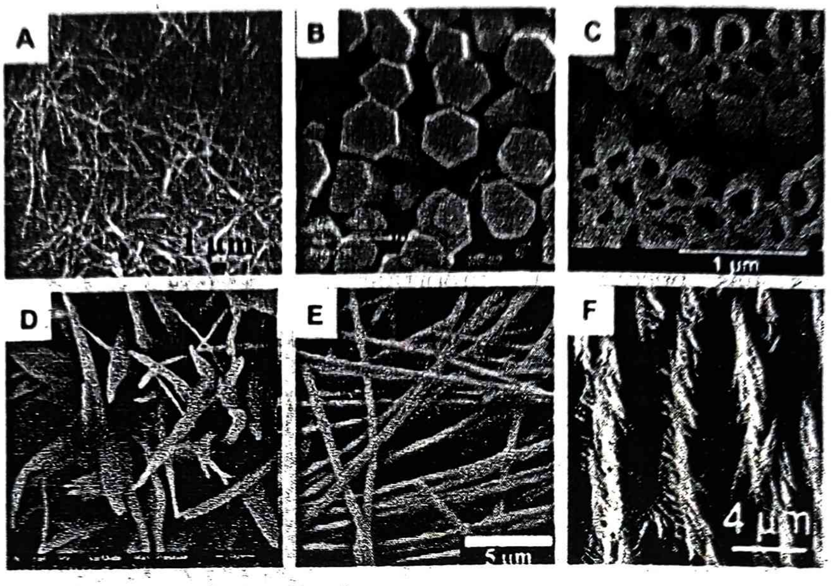

Figure 4: Typical SEM image of different types of 1D nanomaterials: (A) nanowires, (B) nanorods, (C) nanotubes, (D) nanobelts, (E) nanoribbons, and (F) hierarchical nanostructures.

Considerable research has been conducted on new routes to control the synthesis and characterization of 1D nanomaterials. The unique properties of as-obtained 1D nanomaterials can lead to applications in various fields such as electronics, magnetism, optics, and catalysis. Therefore, researchers working in the 1D nanomaterials are constantly striving to develop fundamental discoveries as well as to find the scope of potential applications.

3.3 Two dimensional nanostructures

Two-dimensional (2D) nanomaterials are composed of thin layers which may have a thickness of at least one atomic layer. Contrary to bulk materials, these nanomaterials have a high aspect ratio (surface-area-to-volume ratio) and therefore have many atoms on their surface. These surface atoms have a different function than internal atoms, and the increase in the number of surface atoms leads to a change in the behavior of 2D nanomaterials. 2D nanomaterials can be

1. amorphous or crystalline.

2. made up of various chemical compositions.

3. used as a single layer or as multilayer structures.
4. deposited on a substrate.
5. integrated in a surrounding matrix material.
6. metallic, ceramic, or polymeric.

In recent years, synthesis of two dimensional nanomaterials has become an important area of research in material science. This is owing to their many low dimensional characteristics different from the bulk properties. 2D nanomaterials with certain geometries exhibit unique shape-dependent characteristics and subsequently utilized as building blocks for the key components of nanodevices. In addition, a 2D nanomaterial is particularly interesting for novel applications in sensors, photocatalysts, and nanocontainers, nanoreactors and templates for two dimensional nanostructure materials. Graphene is one of the best example of 2D nanomaterials. It has unique properties that result in its widespread use in various industries. In addition to graphene, other 2D nanomaterials are boron nitride nanosheet (BNNS), transition metal dichalcogenide (TMDC), mono-elemental 2D semiconductors (silicene, germanene, stanene, and phosphorene), MXenes, and 2D oxide/hydroxide materials. These 2D nanomaterials are obtained in the form of branched structures, nanoprisms, nanoplates, nanosheets, nanowalls, and nanodisks. Such structures of 2D nanomaterials are shown in Figure 5.

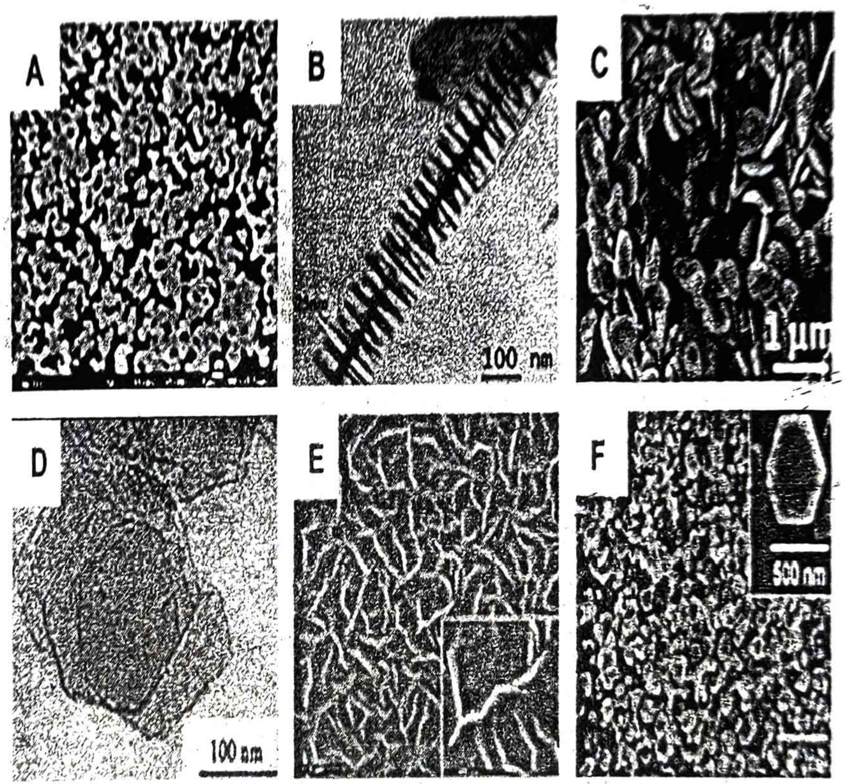

Figure 5: Typical SEM and TEM image of different types of 2D nanomaterials: (A) junctions (continuous islands), (B) branched structures, (C) nanoplates, (D) nanosheets, (E) nanowalls, and (F) nanodisks.

3.4 Three Dimensional Nanostructure Materials

Bulk nanomaterials (three dimensional) are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm. Some of the characteristics features of 3D nanomaterials are:

1. These materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.
2. In terms of nanocrystalline structure, 3D nanomaterials can be composed of a multiple arrangement of nanosize crystals, most typically in different orientations.
3. With respect to the presence of features at the nanoscale, 3D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers.

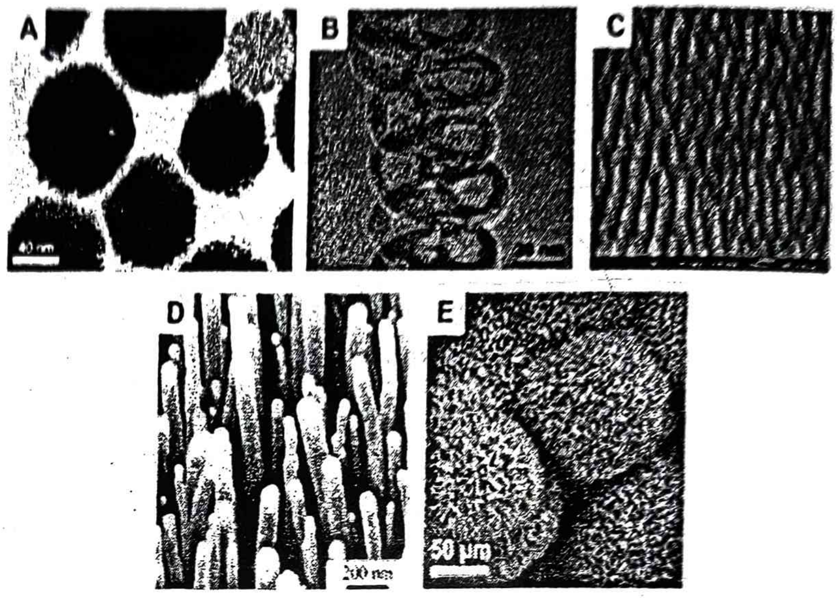

Figure 6: Typical SEM and TEM images of different kinds of 3D nanomaterials: (A) nanoballs (dendritic structures), (B) nanocoils, (C) nanocones, (D) nanopillers, and (E) nanoflowers.

These materials also have large specific surface area and other superior properties over their bulk counterparts. These properties strongly depend on the sizes, shapes, dimensionality, and morphologies and determine the ultimate performance and applications of 3D nanomaterials. 3D nanomaterials are used in various fields such as area of catalysis, magnetic material, and electrode material for batteries. Moreover, 3D nanomaterials have recently attracted intensive research interests because of their higher surface area and capable of supplying enough absorption sites for all involved molecules in a small space. These nanomaterials have porosity within the structure and lead to better transport of molecules. Further, these 3D nanomaterials possess unique optical, electric and magnetic properties which open up possible scope of applications. Some three dimensional nanostructures are shown in Figure 6.

3.5 Nanodots

A NANODOT is defined as a microscopic cluster of several hundred atoms that can be used to store extremely large amounts of data in a computer chip. Hence nanodots can be as small as 50 nanometers (nm) wide and are generally fabricated using electron beam lithography to pattern multilayer thin films. Nanodots are one of two major approaches being pursued around the world as possible means of boosting the density of magnetic data storage. The other one involves using a laser to heat and switch individual bits. Researches are going on to combine these two in increase the data storage capacity.

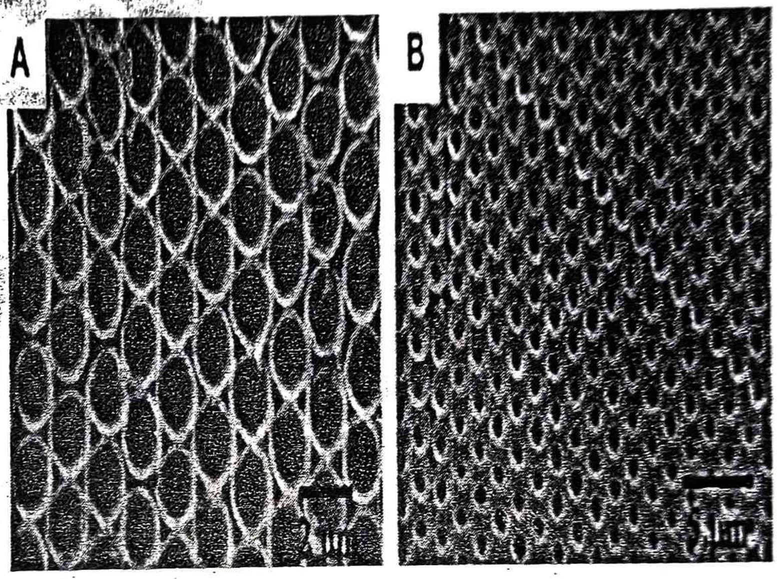

Figure 7: SEM images of ordered gold nano-bowls array at (A) high and (B) low magnification.

Nanodots generally exploit properties of quantum dots to localize magnetic or electrical fields at very small scales. A nanodot has north and south poles like a tiny bar magnet and switches back and forth (or between 0 and 1) in response to a strong magnetic field. Generally, the smaller the dot, the stronger the field required to induce the switch. Until now researchers have been unable to understand and control a wide variation in nanodot switching response. Some of the examples of nanodots are carbon nanodots and permalloy ($Ni_{80}Fe_{20}$) nanodots. The latter one is available in triangular, diamond, and hexagonal shapes. Carbon nanodots are superior because of their water solubility, chemical inertness, low toxicity, ease of functionalization and resistance to photo-bleaching.

Applications for nanodots include high-density information storage, energy storage, light-emitting devices, photo-catalysis, energy conversion, optoelectronics, and especially in sensing. Further the carbon dots are used in bioimaging, drug delivery, microfluidics, sensing, logic gates, and chiral photonics. SEM images of gold nanobowls are shown in Figure 7 with both high (left) and low (right) magnification.

3.6 Thin Films

Modern life would not be possible without thin films and coatings. Thickness of thin film is very small. Due to this, thin films are almost invisible to the naked eye or buried below other surface layers. Nevertheless, their impact on electronic, optical, mechanical or biological functions of a material or device can be tremendous. For example, integrated electronic or data storage devices entirely rely on thin films. Materials science and engineering aspect of thin films comprise also the engineering at the interface. This interface engineering is essential to optimize adhesion and performance of various kinds of thin films. For example, thin films are used in solar cells, packaging foils, electronic devices and in many other applications. Fuel-efficient automobiles require low-friction engine parts with designed thin films. Special coatings are also needed for processing tools such as cutters, drillers and many more. Optical coatings for energy-efficient windows or anti-reflection properties are the fields where thin films find wide applications.

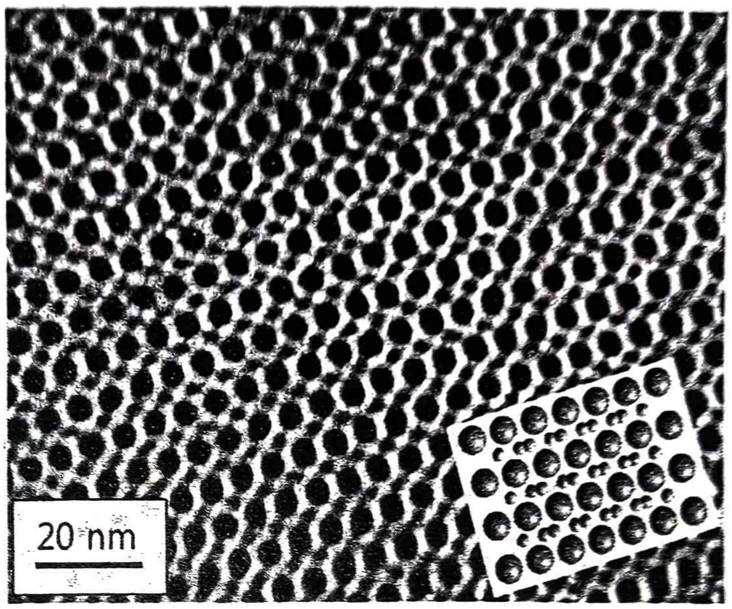

Figure 8: Thin film of binary superlattices from 4.7 nm PbS nanocrystals and 2.5 nm $Mo_{72}V_{30}$ clusters.

A thin film is a layer of material of thickness ranging from fractions of a nanometer (monolayer) to several micrometers. Such thickness is controlled by the deposition technique during the synthesis of thin film and it (deposition) is a fundamental step in many applications. A familiar example of such deposition is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors, while more recently, a metal layer is deposited on the glass surface using techniques such as sputtering. A stack of thin films is called a multilayer. A thin film of binary superlattices from 4.7 nm PbS nanocrystals and 2.5 nm $Mo_{72}V_{30}$ clusters is shown in Figure 8.

An ideal thin film can mathematically be defined as a homogeneous solid material contained between two parallel planes and extended infinitely in two directions (x, y) but restricted along the third direction (z), perpendicular to the $x - y$ plane. The dimension along z-direction is known as the film thickness d. The value of d may vary from a few nanometer to any arbitrary value say to 10 μm or more but always remains much less than those along the other two directions i.e. x and y. The value of d determines the thickness of the film. Thin films possess various physical properties such as electrical, optical, magnetic, and mechanical which depend on several factors like rate of deposition, substrate temperature, environmental conditions, residual gas pressure in the system, purity of the material to be deposited, inhomogeneity of the film, structural and compositional variations of the film in localized or wider areas.

Modern electronic and technological devices are built in thin film form. Some of these devices are monolithic and hybrid circuits, junction field effect transistors (JFET), metal oxide semiconductor transistors (MOST), sensors for different applications, switching devices, cryogenic applications, high density memory systems for computers etc. In addition to their interest in application fields, thin films play an important role in the development and study of materials with new and unique properties. Thin films made of multiferroic materials, and superlattices provide the platform of the investigation of quantum phenomena. Some of the characteristics features of thin films are mentioned below:

1. Thickness of thin film varies from nm to μm.
2. Properties like electrical (resistivity), optical (transmission), mechanical (Young's modulus) and thermal (conductivity) depend on thickness.
3. Structure of thin film may be amorphous, polycrystalline or single crystal.
4. Structure of thin film depends on the method of deposition.
5. Structure of thin film changes with temperature.
6. Thin films suffer severe stresses (tensile or compressive).

3.6.1 Applications of thin films

Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media, electronic semiconductor devices, LEDs, optical coatings (such as antireflective coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin-film solar cells) and storage (thin-film batteries). It is also being applied to pharmaceuticals, via thin-film drug delivery.

3.7 Nanowires

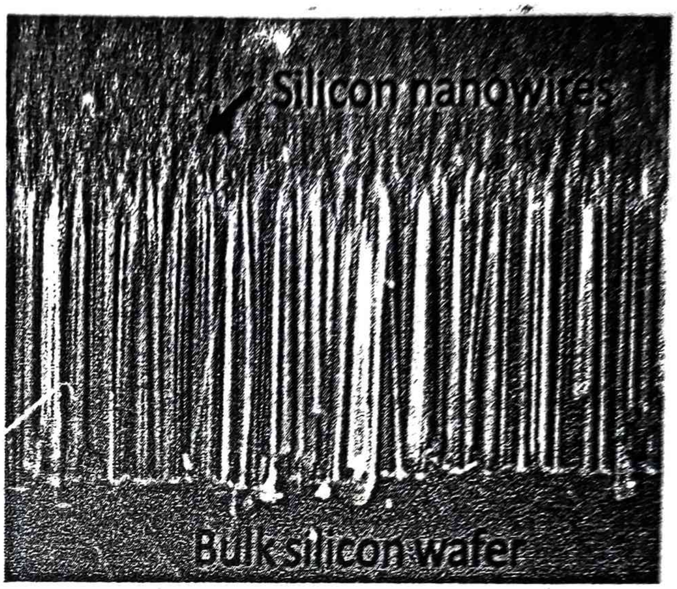

Figure 9: SEM images of silicon nanowires.

A nanowire is a wire of dimension of the order of a nanometer (10^{-9} meters). Nanowires can also be alternatively defined as *structures that have a lateral size constrained to tens of nanometers or less and an unconstrained longitudinal size*. At these scales, quantum mechanical effects become dominant hence such wires are also known as "quantum wires". Nanowires are just like normal electrical wires but they are extremely small. This makes the big difference between conventional wire and a nanowire. Nanowires are fabricated in various forms such as metallic (e.g., Ni, Pt, Au), semiconducting (e.g., InP, Si, GaN, etc.), and insulating (e.g., SiO_2, TiO_2). Molecular nanowires are also composed of repeating molecular units either organic or inorganic. Nanowires are also made from carbon nanotubes. As an example, silicon nanowires are shown in Figure 9. These nanowires are grown on bulk silicon wafer used as substrate.

Nanowires have diameters less than or equal to 100 nanometers. The first nanoscale quantum-well wire (a thinly layered semiconductor structure) was developed in 1987 by scientists at Bell Laboratories. A nanowire of more-refined design was developed and described in 1991 by Belgium engineer Jean-Pierre Colinge. Since then, nanowires have been investigated for possible applications in many fields, including optics, electronics, and genetics.

Nanowires can be made from a wide variety of materials including semiconductors like silicon, germanium, carbon, and various conductive metals such as gold and copper. Their small size makes them good conductors with electrons passing easily through them. This property has allowed for important advances in computer science. For example, it has been possible to develop an optical photonic switch using specialized cadmium sulfide nanowires that allow photons to pass through the wire and act as binary signals (i.e., 0 and 1). This feature has the potential to enhance greatly the computer speed.

In genetics, researchers have used nanowires to create artificial protein-coding DNA. Such nanowires are formed using amino acids, which are the building blocks of proteins, and DNA. This technology is used to facilitate the creation or production of proteins, and thereby advances the protein research. This leads to a potential advancement in therapeutic applications, such as for the replacement or repair of dysfunctional proteins.

3.7.1 Nanowire Size

Nanowires are less than 100 nanometers in diameter and can be as small as 3 nanometers. Aspect ratio (AR) of a nanowire is defined as the ratio of length to diameter and plays a significant role in such one dimensional nanostructure. Nanowires have typically AR=1000. Generally, an aspect ratio below 10 corresponds to nanorods, while an AR above 10 corresponds to a nanowire but there is no such fixed classification. This massive difference in the length to diameter ratio indicates that nanowires can be treated as one dimensional materials. Due to the high aspect ratio, nanowire arrays with low density are relatively fragile and thus unable to withstand the pressures that are normally applied to macroscopic and even thin films of nanowire.

3.7.2 Quantum Mechanical Effects

The minute size of nanowires means that quantum mechanical effects become important. "Quantum wires" exploit quantum mechanics to produce wires with a range of unique electrical properties. These properties include quantum tunneling that allows wires made from carbon nanotubes to have extremely high conductivity with electrons traveling ballistically through the wire.

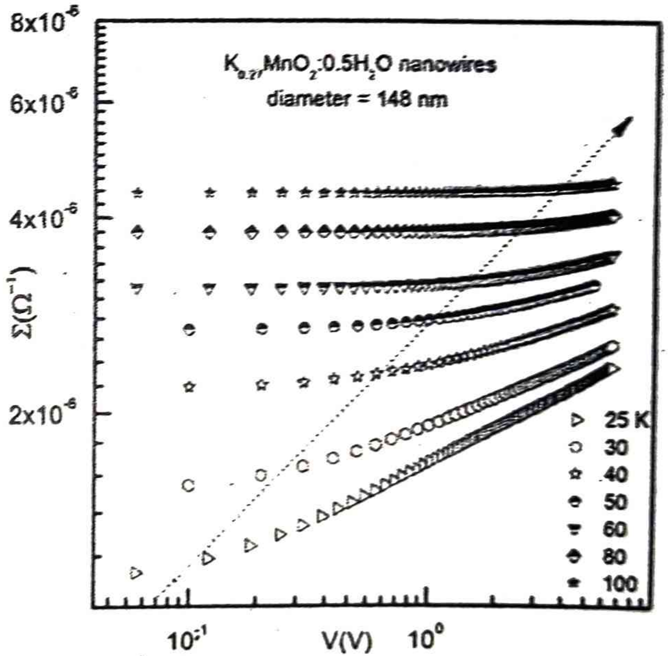

Figure 10: Variation of conductance of $K_{0.27}MnO_2 : 0.5H_2O$ nanowire of diameter 148 nm at different temperatures mentioned in the graph.

3.7.3 Nanowire conductivity

When the width of the nanowire is less than the mean free path of free electrons of the wire material, electrons experience defects, edge effects and suffer scattering. This indicates that nanowires made from metals can have conductivity much lower than that for the bulk material. Such conductance does not behave linearly with voltage like an Ohmic conductor (at least up to a certain voltage) rather it shows nonOhmic character.

Non-Ohmic conduction is a common feature of the low-dimensional nanotubes and nanowires. Such variation in conductance for a $K_{0.27}MnO_2 : 0.5H_2O$ nanowire of diameter 148 nm at different temperatures is shown in Figure 10. For a small applied voltage V, conductance $\Sigma(V)$ at a fixed temperature remains almost constant to its zero-voltage Ohmic value Σ_0. However with the increase in V, $\Sigma(V)$ increases from Σ_0 exhibiting the nonOhmic characteristics. The value of V at which $\Sigma(V)$ deviates from Σ_0 for the first time is known as the onset voltage V_0 and the corresponding current is known as the onset current I_0. With further increase in voltage beyond V_0, the conductance increases monotonically indicating nonOhmic behaviour as a function of V.. Similar nonOhmic transport behaviour of conductance with voltage is also observed at other temperatures. It is observed from Figure 10 that V_0 *decreases* with decreasing temperature up to the measured range of temperature. This is clearly seen by the orientation of the dotted line in Figure 10.

3.7.4 Applications of Nanowires:

The interesting physical properties of nanowires have led extensive potential applications in several fields. Some of the applications of nanowires are as follows:

1. These nanowires are used to make connection in exceptionally small electronic circuits.
2. These nanowires are used in memory devices and quantum devices.
3. Using nanowires, transistors are built without p-n junctions.
4. Nanowires are used in advanced composite materials, biomolecular nanosensors, micro-electromechanical systems (MEMS) and in photoelectronics.
5. They are used in field emitters and photon ballistic waveguides.
6. Nanowires are used in heterostructure which are sub divided as axial hetrostructure for ex- Gap-GaAs, radial hetrostructure ex- SiGe and nano superlatticles.
7. Nanowires are mostly applicable in sensors like ph sensor and gas sensor. They are used as efficient sensors for detecting minute amount of toxic gases, chemical weapons and explosives etc.
8. Used in the manufacturing of nanophotons and nanoprobes with high temperature and high laser technology.
9. Due to the very small shape, nanowire materials are used in making electrical connections in the devices with the outside world.

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10. Reliable methods exist for their parallel assembly.

11. Perhaps the most obvious use for nanowires is in electronics. Some nanowires are very good conductors or semiconductors, and their miniscule size means that manufacturers could fit millions more transistors on a single microprocessor. As a result, computer speed would increase dramatically.

12. Nanowires may play an important role in the field of quantum computers. A team of researchers in the Netherlands created nanowires out of indium arsenide and attached them to aluminum electrodes. At temperatures near absolute zero, aluminum becomes a superconductor and the nanowires also became superconductors due to the proximity effect. The researchers could control the superconductivity of the nanowires by running various voltages through the substrate under the wires.

13. Nanowires may also play an important role in nanosize devices like nanorobots. Doctors could use the nanorobots to treat diseases like cancer. Some nanorobot designs have on board power systems, which would require structures like nanowires to generate and conduct power.

14. Using piezoelectric material, it is possible to create nanowires that generate electricity from kinetic energy. The piezoelectric effect is a phenomenon in which certain materials emit electric charges when a physical force is applied to a piezoelectric material. If an electric charge is given to this same material, it vibrates. Piezoelectric nanowires might provide power to nanosize systems in future, though at present there are no practical applications.

15. There are hundreds of other potential nanowire applications in electronics. Researchers in Japan are working on atomic switches that might some day replace semiconductor switches in electronic devices. Scientists hope that coaxial nanowires will improve the energy efficiency of solar cells.

16. Nanowires have tunable optical and electrical properties and hence can be used in low cost and high efficiency solar cells.

17. Zinc oxide nanowires are used in the detection of chemical vapors.

18. Silver nanowires embedded in a polymer are used to make conductive layers that can flex without damaging the conductor.

3.8 Nanorods

In nanotechnology, nanorods have the morphology of nanoscale objects. Each of their dimensions range from $1-100\ nm$. They are synthesized from metals or semiconducting materials by direct chemical route. Standard aspect ratios of such nanorods (length divided by width) are 3 to 5. A combination of ligands act as shape control agents and bond to different facets of the nanorod with different strengths. This allows different faces of the nanorod to grow at different rates, producing an elongated object.

3.8.1 Different types of nanorods

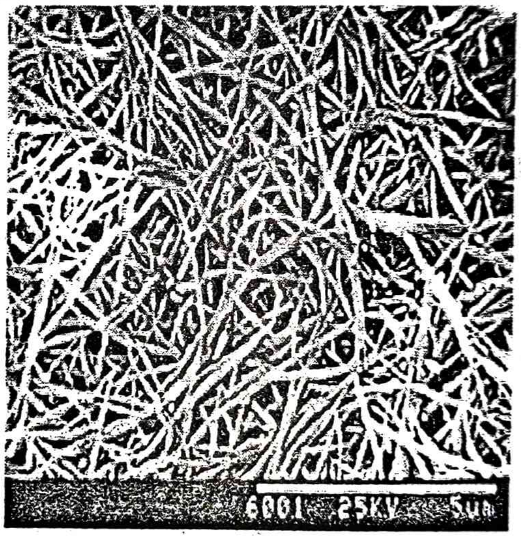

Figure 11: Carbon nanorods.

Various types of nanorods such as carbon nanorods, ZnO nanorods, gold nanorods and magnetic nanorods are being fabricated and studied extensively. Recently, various techniques have been proposed for synthesizing the nanorods. It can be classified into either via physical or chemical methods or via bottom-up or top-down techniques. Various techniques of synthesis of nanorods are thermal hydrolysis, hydrothermal route, sol-gel, vapor condensation, spray pyrolysis, pulse laser decomposition, laser ablation, thermal evaporation, pulse combustion-spray pyrolysis, electro-mechanical, flame spray plasma, microwave plasma, low energy beam deposition, ball-milling, chemical vapor deposition, laser ablation, chemical reduction, co-precipitation, hybrid wet chemical route, physical evaporation, electrophoretic deposition, radio frequency (RF) magnetron sputtering, vapor deposition, metal assisted growth, template assisted routes, metal-assisted growth and seed-based growth, simple chemical etching, etc. Nanorods are prepared by controlling the nucleation growth along the longitudinal direction rather than transverse one.

region (NIR). Small change in aspect ratio will result in drastic change in the NIR absorption wavelength. The gold nanorods could be synthesized via two general growth approaches, which are bottom-up and top-down methods. TEM images of gold nanorods are shown in Figure 13. For bottom-up methods, Au nanorods are generated through nucleation in aqueous solutions and subsequent overgrowth, where Au salts are usually used to provide the Au source through reduction. Particularly, bottom-up method including wet-chemical, electrochemical, sonochemical, solvothermal, microwave-assisted and photochemical reduction technique. All of these method involving the use of reduced aqueous solvated gold salts by various reducing agents, such as sodium borohydride, ascorbic acid, and small Au clusters, under different external stimuli (triggering the reduction of gold salt). The length of Au nanorods could be elongated with the use of template, it serves to confine the growth along one direction during the reduction.

3.8.5 Magnetic nanorods

Nanostructured iron oxide magnetite (Fe_3O_4) shows supermagnetic property and are widely used in biomedical field and in device applications. The magnetic nanoparticle are generally utilized as nano-adsorbents in cancer diagnostic and treatment, and as contrast agent in magnetic resonance imaging (MRI). It is worth mentioning that 1D magnetite is extremely important in the building block for nanodevices. The size and shape of magnetite nanoparticles play a key role in controlling the corresponding properties. These nanoparticles are synthesized via aqueous coprecipitation, magnetic field induction, CVD, template mediated, etc. The aqueous coprecipitation of Fe^{2+} and Fe^{3+} by a base, usually sodium hydroxide or aqueous ammonia, is the well-known method which is usually carried out for synthesizing the magnetite nanoparticles. This method is the most scalable chemical synthesis routes which results in iron oxide nanospherical crystal. Figure 14 shows $Fe(III)$ oxide hydroxide nanorods of particle size 10 nm.

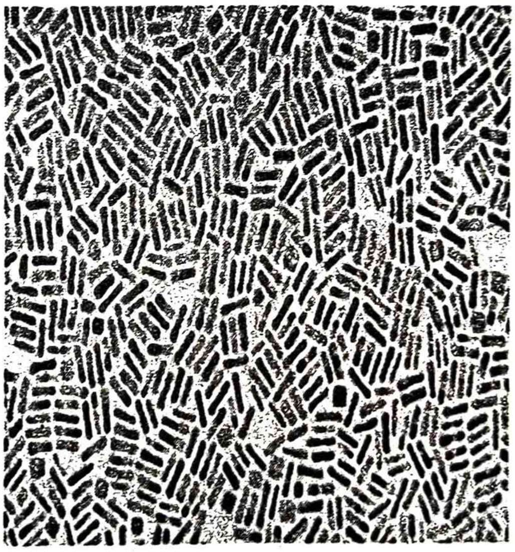

Figure 14: Fe(III) oxide hydroxide nanorod of particle size 10 nm.

Recently, considerable attention has been paid for the production of 1-D magnetite nanorods. This is because of their high surface to volume ratio and superior properties. Magnetic nanorods have very high values of coercivity because of their high aspect ratio. These materials also produce a lot of heat in high frequency magnetic field, which offer longer blood circulation times, stronger interaction with tumors, enhanced retention at tumor sites and improved targeting efficiency. Such excellent practical applications of the magnetic nanorods have stimulated their mass production as targeting pharmaceutical carrier or MRI contrast agents. For example, iron oxide nanocubes including nanorods structure with a length larger than 100 nm could be achieved via thermal decomposition, wet chemical, hydrothermal, template mediated, solvo-thermal, hydrolysis and sol-gel.

3.8.6 Advantages of nanorods

Nanorods have anisotropy in shape. The nanorods serve as attractive components for many applications. It has been discovered that the nanorods are highly efficient as compared to spherical particles. This is due to the increase in aspect ratio of the particles which in turn leads to an increase in excitation of surface plasmons in the nanoparticles. This increase in surface plasmons increases the strength of the dipole moment within a nanoparticle leading to an enhancement of electrical field in a nanorod as compared to spherical particles. One example of such benefit of a rod-like shape of nanorod has been demonstrated by Alivisatos and co-workers who observed partial alignment of $CdSe$ nanorods providing an effective, directed path for charge carriers to move throughout the photovoltaic device.

Further, the incorporation of nanorods within P3HT film improves the external quantum efficiency by a factor of 3 as the aspect ratio in this case increases from 1 to 10. The accumulation of electrons is also improved as the aspect ratio of nanoparticles increases. Furthermore, alignment of nanorods also plays a key role in improving its properties. It has been experimentally demonstrated that the electrical conductivity of Ag nanorods and polystyrene composites is greatly affected by the aspect ratio of anisotropic nanoparticle in the polymer composites. In such composites, theory of percolation is applied to explain the variation of electrical conductivity as a function of volume fraction of the nanorods. Conduction through percolation is found to depend on both size and shape of the nanoparticles. The percolation threshold becomes minimal due to the rod-shape particles as compared to spherical particles. Further various orientation properties of the nanorods are found to rely on the larger values of both length and diameter of rod-shape particles. Hence, it can be summarized that the efficiency of nanorods depends strongly on the aspect ratio, volume fraction, polydispersity and orientation.

3.8.7 Applications of nanorods

Nanorods are widely used in many potential applications. Some of them are summarized below.

1. Nanorods are used as biosensor, magneto-electronic, magneto-sensor, nanotransistor, data storage media, microwave electronic devices in high frequency region, etc.

2. Nanorods are used in display technologies, because the reflectivity of the rods can be changed by changing their orientation with an applied electric field.

3. Another application is for micro-electromechanical systems (MEMS). Nanorods, along with other noble metal nanoparticles, also function as theragnostic agents.

4. Nanorods absorb light in the near IR, and generate heat when excited with IR light. This property has led to the use of nanorods as cancer therapeutics.

5. Nanorods can be conjugated with tumor targeting motifs and ingested. When a patient is exposed to IR light, nanorods selectively taken up by tumor cells are locally heated, destroying only the cancerous tissue while leaving healthy cells intact.

6. Nanorods based on semiconducting materials are also being used as energy harvesting and light emitting devices.

4 Band Structure of materials at nanoscale

Band structure is one of the most important concepts in solid state physics. It provides the electronic levels in (ideal) crystal structures, which are characterized by two quantum numbers, the Bloch vector $\vec{k}$ and the band index n. Here the Bloch vector $\vec{k}$ is an element of the reciprocal space (in units 1/length) and the energy of the electron $E_n(\vec{k})$ is a continuous function of $\vec{k}$, so that one obtains a continuous range of energies referred to as the energy band. Many electrical, optical, and even some magnetic properties of crystals can be explained in terms of the band structure. Of particular importance is the location of the Fermi energy, up to which all levels are occupied at zero temperature. If the Fermi energy is located in a band gap, the material is insulating (or semiconducting) while it is metallic otherwise.

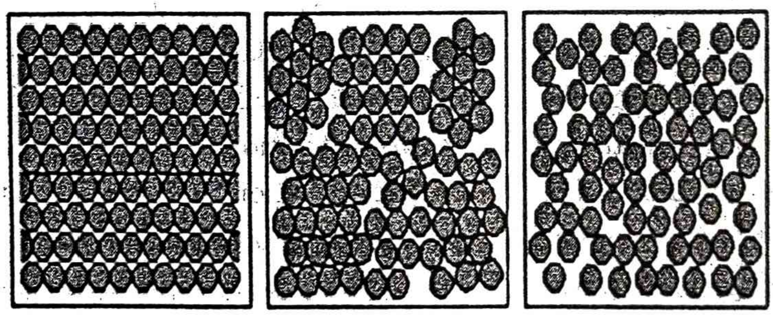

Figure 15: Single crystal which is periodic across the whole volume (left), polycrystal which is periodic across each grain (middle) and amorphous solids, not periodic (right).

4.1 Single crystal, polycrystal and amorphous materials

Materials are generally classified as single crystals, polycrystals and amorphous. These three categories are described below in brief.

Single Crystal: An ideal single crystal has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry. A single crystal often has distinctive plane faces and some symmetry. The actual shape of the crystal will be determined by the availability of crystallizing material, and by interference with other crystals, but the angles between the faces will be characteristic of the material and will define an ideal shape. Single crystals showing these characteristic shapes can be grown from salt solutions such as alum and copper sulphate. Model structure of single crystal is shown in the left panel of Figure 15.

Gemstones are often single crystals. They tend to be cut artificially to obtain aesthetically pleasing refractive and reflective properties. This generally requires cutting along crystallographic planes. This is known as cleaving the crystal. A familiar example is diamond, from which decorative stones can be cleaved in different ways to produce a wide range of effects.

Polycrystal: A polycrystalline solid or polycrystal is comprised of many individual grains or crystallites. Each grain can be thought of as a single crystal, within which the atomic structure has long-range order. In an isotropic polycrystalline solid, there is no relationship between neighboring grains. Therefore, on a large enough length scale, there is no periodicity across a polycrystalline sample. Unit cells are in random directions. In the middle panel of Figure 15, a polycrystalline sample is shown.

Single crystals form only in special conditions. The normal solid form of an element or compound is polycrystalline. As the name suggests, a polycrystalline solid or polycrystal is made up of many crystals. The properties of a polycrystal are notably different from those of a single crystal. The individual component crystallites are often referred to as grains and the junctions between these grains are known as grain boundaries .

The size of a grain varies according to the conditions under which it formed. Galvanized steel has a zinc coating with visibly large grains. Other materials have much finer grains, and require the use of optical microscopy. The three-dimensional shape of grains in a polycrystal is similar to the shape of individual soap bubbles made by blowing air into a soap solution contained in a transparent box.

The surface between bubbles is a high-energy feature. If the area of the surface is decreased, the overall energy of the system decreases, so reduction of surface area is a spontaneous process. If all the bubbles were of same size, the resulting structure would be a regular close-packed array, with 120^o angles between the surfaces of neighboring bubbles. In practice, bubble growth can occur because the surface area of a few large bubbles is lower than that of many small bubbles.

Large bubbles tend to grow, and small bubbles tend to shrink. The bubbles are therefore different sizes so there are large deviations from the close-packed structure. On average, however, three bubbles meet at a junction, and the angle between the bubble surfaces is usually within a few tens of degrees of 120°. The curvature of the surfaces is also important. Surfaces with a smaller radius of curvature have a higher energy than those with a larger radius of curvature. As a result, some small bubbles cannot shrink and disappear, even though the surface area would decrease if they did so. This is because the curvature of the boundaries, and the associated energy, would be too high.

In a real polycrystal, the grain boundaries are high-energy features, similar to the surfaces between bubbles. The soap froth is a very good model for the grain structure of a simple polycrystalline material, and many similar features can be observed in the two systems. The soap bubbles are analogous to the grains, and the surfaces of the bubbles are analogous to the grain boundaries. Compare the photographs of the soap bubbles with the micrograph of a polycrystalline material that has been etched to reveal the grain boundaries.

Amorphous materials: These materials, like window glass, have no long-range order at all, so they have no translational symmetry. The structure of an amorphous solid (and indeed a liquid) is not truly random - the distances between atoms in the structure are well defined and similar to those in the crystal. This is why liquids and crystals have similar densities - both have short-range order that fixes the distances between atoms, but only crystals have long-range order. In the right panel of Figure 15, an amorphous sample is shown.

Within a single crystal or grain, the crystal structure is not perfect. The structure contains defects such as vacancies , where an atom is missing altogether, and dislocations , where the perfection of the structure is disrupted along a line. Grain boundaries in polycrystals can be considered as two-dimensional defects in the perfect crystal lattice. Crystal defects are important in determining many material properties, such as the rate of atomic diffusion and mechanical strength.

4.2 Band structure of single crystal materials

A band structure is a 2D representation of the energies of the crystal orbitals in a crystalline material. Sometimes referred to as "spaghetti diagrams", a band structure plot can quickly reveal whether a material is metallic, semi-metallic, or insulating, and for those materials with band gaps whether they are direct or indirect as well as the magnitude of the gap. Additionally, the curvature of the bands can reflect the carrier mobility through those bands. A sample band structure for silicon is shown in Figure 16. As no bands cross from the valence band (bottom set of bands) to the conduction band (top set of bands), Si is a semiconductor with a band gap of about 1.11 eV (based off of this calculation). As the conduction band minimum (orange dot) and the valence band maximum (blue dots) are not vertically aligned, the band gap is indirect.

While one is able to quickly determine many materials properties by examining a band structure diagram, an intuitive understanding of how the band structures arise and why they are presented in such ways requires deeper study. The energies of the bands are calculated in "k-space" or sometimes called "momentum space". This is an abstract space intimately related to real, or position space.

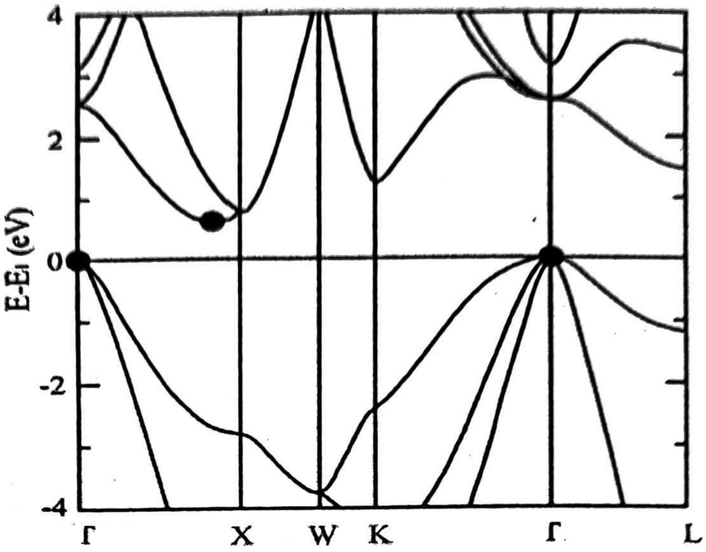

Figure 16: Band structure of elemental Si calculated using density functional theory (DFT). The blue circles represent the valence band maximum and the orange circle is the conduction band minimum. The band gap of approximately 1.11 eV can be seen through the difference in energy (y-axis) at these two points. As the valence band maximum and conduction band minimum are not vertically aligned, the band gap is indirect.

4.3 Band structure of one dimensional chain of atoms

In this section, we show how periodic conditions on a crystal result in quantum states which can be expressed conveniently in discrete wave numbers which are related to the wavelengths of the crystal orbitals. The energies of the states characterized by these wave numbers can be calculated and plotted giving rise to an orbital band, forming the basis for electronic structures of more complicated crystals. We assume a one dimensional chain of N atoms separated by a lattice spacing a each with just one valence s orbital. A periodic boundary condition is imposed so that the N^{th} atom interacts with the 1^{st} atom of an adjacent chain. Thus,

$$\Psi(x) = \Psi(x + Na) \tag{2}$$

Since the electron density must be unchanged with each lattice spacing as the chain is uniform, we have $\rho(x+a) = \rho(x)$ and knowing $\rho(x) = \Psi^*(x) \times \Psi(x)$ which must be real, it must be that $\Psi(x+a) = \mu\Psi(x)$ where μ is a complex number such that $\mu^*\mu = 1$. Thus,

$$\Psi(x + Na) = \mu^N \Psi(x) \tag{3}$$

with $\mu^N = 1$ to satisfy equation (2) so

$$\mu = e^{\frac{2\pi p}{N}} = cos\left(\frac{2\pi p}{N}\right) + isin\left(\frac{2\pi p}{N}\right). \tag{4}$$

Here p is a quantum number that must span the integers from $-N$ to N. We can define the wave vector k such that $k = \frac{2\pi p}{Na}$. k is now a quantum number with units of inverse length that is dependent on the number of atoms in the crystal. For any reasonably large N, k is functionally continuous. We can now write that

$$\Psi(x+a) = e^{ika}\Psi(x). \tag{5}$$

and see a solution to the wavefunction as

$$\Psi(x) = e^{ikx}. \tag{6}$$

By taking into equation (5), we can further generalize the wave function assuming a periodic function $u(x) = u(x+a)$ as

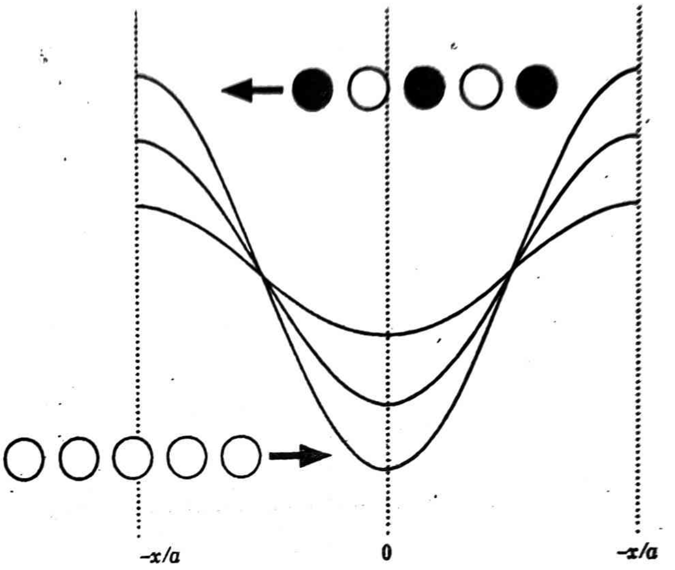

Figure 17: Band structure of one dimensional chain of atoms. $k = 0$ corresponds to an infinite crystal orbital wavelength with all the orbitals in phase. As k deviates from 0, the wavelength gets smaller as nodes are introduced until it reaches a minimum at $k = \pm\frac{\pi}{a}$ corresponding to each orbital completely out of phase with its neighbors.

$$\Psi(x) = e^{ikx}u(x). \tag{7}$$

This is the familiar Bloch function. Thus, we see that the wavefunction is a combination of the periodic potential $u(x)$ on each atom with an exponential term that varies with the wavenumber $\vec{k}$.

As shown in Figure 17, at $k = 0$, the orbitals are all in phase with each other leading to no nodes between them and an infinite crystal orbital wavelength. As k moves from 0, nodes are introduced into the chain when some orbitals switch phases until $k = \pm\frac{\pi}{a}$ at which every orbital is out of phase with its neighbors. This leads to a minimum crystal orbital wavelength of $2a$. Now seeing how k arises in a crystal due to a periodic potential, we can use a linear combination of atomic orbitals approach to calculate the energy of the chain with varying k to see how a band develops.

Thus we see that the energies of a one dimensional chain of atoms can be calculated easily with some approximations as the band structure is rather simple. A real band structure consists of many bands corresponding to all of the orbitals on all of the atoms in the unit cell. In order to obtain the more complicated band structures of real materials, it can help to extend our images of crystal wavelengths to higher dimensions and with orbitals other than s. Quantitatively calculating the energy is infeasible and requires computational programs, though a qualitative understanding can be further developed.

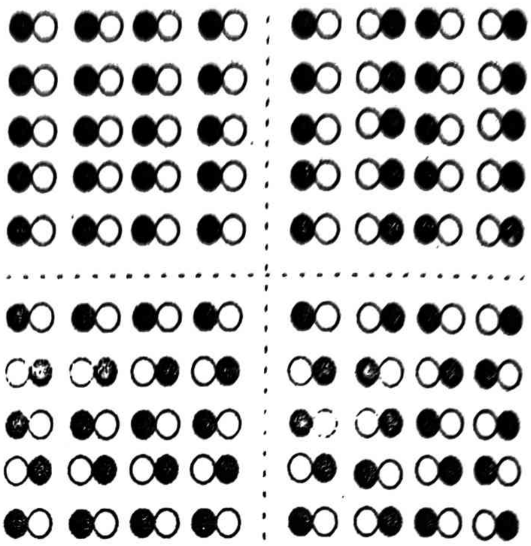

Figure 18: A hypothetical two dimensional lattice consisting of one p orbital per atom. The crystal orbital arrangements for $4k$ vectors are shown. The lowest energy k vector, $k = (\frac{\pi}{a}, 0)$ has the orbitals in the most bonding arrangement in the x and y directions. $k = (0, \frac{\pi}{a})$ is the most antibonding arrangement and the highest energy.

Figure 18 shows a hypothetical two dimensional lattice consisting of a p orbital on each atom. In two dimensions we move from a wavenumber to a wave vector. When k = (0, 0) the crystal orbital wavelength is infinite in both directions as the orbitals do not switch phase throughout the crystal. For the chain of s orbitals this was the most stable energy. However in this case, the orbitals are most stabilized in the y direction (adjacent orbital overlap is in phase in the y direction) and destabilized in the x (adjacent orbital overlap out of phase in the x direction). This model highlights the intricacies of band structure calculations as both the orbital phases and the relative orbital overlap in each direction must be considered in order to calculate an energy for a discrete k vector. In this case, the s bonding of the p orbitals in the x direction is stronger than the p bonding in the y, and thus it is not the most stable configuration. We see that for $k = (\frac{\pi}{a}, 0)$, the orbitals have the most favorable interactions in both directions as adjacent orbitals have overlap that is completely in phase, leading to the lowest energy configuration. At $k = (-\frac{\pi}{a}, \frac{\pi}{a})$ the orbitals have favorable overlap in the x direction, and at $k = (0, \frac{\pi}{a})$ the orbitals are most antibonding (adjacent orbitals out of phase) leading to the highest energy k vector. This crystal would be further complicated if we did not have a square lattice, but a rectangular lattice with two different lattice vectors.

From this hypothetical lattice, it becomes easier to appreciate the features of real band structures. One must consider orbital interactions in three dimensions arising from s, p, d, and potentially f orbitals on each atom. This leads to complex energy landscapes with many bands.

Moving into 3 dimensions, the set of all unique k vectors comprises the Brillouin Zone (BZ) of the crystal. The BZ exists in reciprocal space and is directly related to the real space lattice. Due to the periodicity of the lattice and Bloch functions, every k vector is equivalent to a k vector inside this BZ and the electronic band structure can be determined solely by calculating energies within the BZ. In the case of our one dimensional chain of atoms, the BZ would be $(-\frac{\pi}{a}, \frac{\pi}{a})$. In three dimensions, the Brillouin Zone is a primitive unit cell in k-space directly related to the unit cell of the real crystal.

As an example, Brillouin Zone of a face-centered cubic lattice is given in Figure 19. The basis vectors in k-space are given by $\vec{b_1}$, $\vec{b_2}$, and $\vec{b_3}$. The marked points labeled G, L, K, etc. correspond to high symmetry points in the Brillouin Zone. In order to calculate the band structure, a path through the Brillouin Zone must be chosen to best capture the energy landscape in three dimensions. Typically, this is done by following the high symmetry points in the Brillouin Zone. The labels given on the x-axis in typical band structure plots correspond to these high symmetry points and the path chosen. Lower symmetry crystals require more extensive paths to accurately capture the electronic structure.

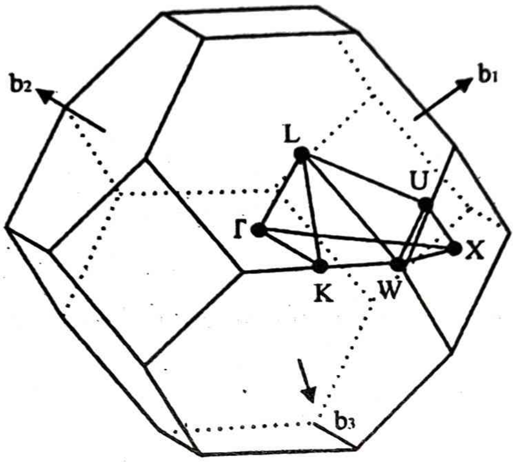

Figure 19: Brillouin Zone of a face-centered cubic crystal. The basis vectors are given by $\vec{b_1}$, $\vec{b_2}$, and $\vec{b_3}$, and labeled points correspond to points of high symmetry in the Brillouin Zone. Paths through k-space dictated by these points accurately capture the whole energy landscape.

4.4 Band gap of nanomaterials

Band gap is one of the leading and important properties of semiconductors. Band gaps play a fundamental role in electrical and optical properties of semiconductor materials. So, it is significant and essential to study the band gap expansion of the semiconductor compound nanomaterials (SCN) to understand the better way of their properties. Semiconductors have extensive applications due to their widen band gap. Bulk silicon is limited in the application due to its indirect and small band gap, whereas Si photon nanodevices have been widely produced and used. Size-dependent band gap has been carried by many experimental and theoretical researchers. The diameter dependence of the effective band gaps in the wires is generally determined from X-ray photoemission spectroscopy and by photoluminence spectra.

Figure 20 shows the variation of band gap of nanomaterials with the diameter of particles. It is clearly observed from the Figure 20 that with the increase in diameter, band gap decreases.

Results of several theoretical models are also shown with the experimental results.

Due to quantum confinement effect, electrons and holes in the semiconductors in nanoscale are confined. Therefore, the energy difference between the filled states and the empty states increases. This widens the band gap of the semiconductor. In optoelectronic devices, this larger band gap drastically changes the optical and electronic properties of semiconductors at nanoscale.

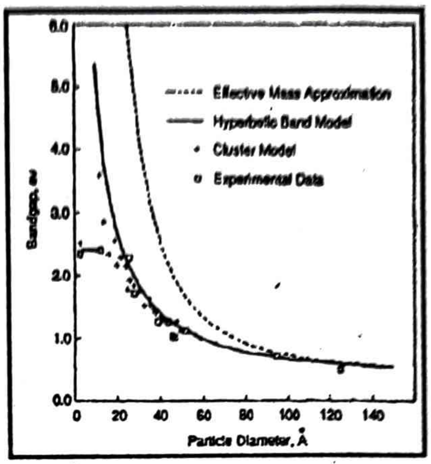

Figure 20: Variation of band gap of nanomaterials with particle diameter.

5 Density of States of materials at nanoscale

It is well known that as per band theory of solids in condensed matter physics, N atoms with N atomic orbitals form N molecular orbitals. Each molecular orbital can take two electrons (opposite spin) so that there are a total of $2N$ energy states. These energy states are discrete but for large values of N, the spacing between them are so small that they can be considered to be continuous forming a continuous energy band. Density of states (DOS) is defined as the number of available energy states per unit energy per unit volume. The units of DOS are $J^{-1}m^{-3}$ or $eV^{-1}cm^{-3}$ and the dimension of DOS is $M^{-1}L^{-5}T^{2}$. DOS provides information on how the energy states are distributed in a given solid. It is typically denoted as $g(E)$ at an energy E. The density of states of a given material can be measured experimentally by photo electron spectroscopy or scanning tunneling microscopy (STM) or electron energy loss spectroscopy (EELS). These techniques probe the density of empty or filled states around the Fermi energy, called local density of states (LDOS). The density of states of a given material can also be calculated by density functional calculations.

The density of states of a system describes the number of states that are to be occupied by the system at each level of energy. It is mathematically represented as a distribution by a probability density function, and it is generally an average over the space and time domains of the various states occupied by the system. The density of states is directly related to the dispersion relations of the properties of the system. High DOS at a specific energy level means that many states are available for occupation.

DOS is a measure of how close together the energy levels are to each other. The density of states can be used to calculate the total number of electron in a band. If $g(E)$ is the DOS, then the total number of electrons in a band, $N(E)$ is given by the equation

$$N(E) = \int_{E}^{top} g(E)\, dE \tag{8}$$

where the integration is performed over the entire energy band. This equation (8) assumes that the probability of occupation of the state is 1. This is not always true when we look at the conduction band of a semiconductor, where the occupation probability is defined by a Fermi function. An energy expression for the density of states, $g(E)$, will be useful for evaluation of the integral in equation (8).

In three dimensions, it is equal to the number of electron states per unit volume per unit energy interval. The calculation of physical properties like conductivity, absorption, emission, and the general distribution of electrons in a material requires the knowledge of density of states. Various bulk properties of materials such as specific heat, paramagnetic susceptibility, and other transport phenomena of conductive solids depend on the density of states. The behaviour of DOS also depends on the dimensionality of the system. We can extract useful physical information about electronic structure of 3D (bulk), 2D (quantum well), 1D (quantum wire) and 0D (quantum dot) materials. The density of states can be used to determine the spacing between energy bands in semiconductors. Depending on the quantum mechanical system, the density of states can be calculated for electrons, photons, or phonons, and can be given as a function of either energy or the wave vector k. To convert between the DOS as a function of the energy and the DOS as a function of the wave vector, the system-specific energy dispersion relation between E and k must be known.

5.1 Density of States in a 3D uniform solid material

To simplify the calculation for $g(E)$ consider a 3D solid with uniform potential. This is a simplification of a real solid but is a good approximation of the valence band of metals where the electrons are loosely bound to the atom and are delocalized. We will also use this approximation for electrons and holes near the edge of the band. For simplicity the uniform potential can be taken to be zero. For this solid the electron is defined by 3 quantum numbers (n_1, n_2, n_3) and its energy is given by

$$E = \frac{h^2}{8m_e L^2}\left(n_1^2 + n_2^2 + n_3^2\right). \tag{9}$$

Equation (9) is for a cubic solid of length L with the three quantum numbers for the three axes. m_e is the free electron mass. We can replace the three quantum numbers by a single value

n so that equation (9) is modified into

$$E = \frac{h^2 n^2}{8 m_e L^2}. \tag{10}$$

For small values of n, these energy levels are quantized, but for large values of n the spacing between them are close so that the energy levels can be considered to be continuous. So n represents the radius of a sphere, where the total number of states within the sphere is given by its volume. This is shown schematically in Figure 21. Since the quantum numbers can only be positive (the quantum numbers represent the electron wave function and it can be shown that to avoid exponential increasing functions the quantum numbers have to be non-zero positive integers) we can only take the first quadrant of the sphere.

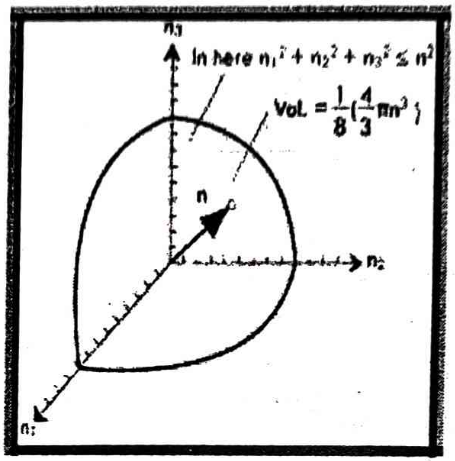
n_3
In here $n_1^2 + n_2^2 + n_3^2 \leq n^2$
Vol. $= \frac{1}{8}(\frac{4}{3}\pi n^3)$
n
n_2
n_1

Figure 21: Energy states in a solid with uniform potential. The portion of the sphere corresponds to the constant energy surface.

Hence the total number of orbitals (energy states), $g_{orb}(n)$, is given by the volume of the sphere in the first quadrant

$$S_{orb}(n) = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right) = \frac{1}{6}\pi n^3. \tag{11}$$

Since each orbital can take two electrons of opposite spin, the total number of energy states (including spin), $S(n)$, is given by

$$S(n) = 2S_{orb}(n) = \frac{1}{3}\pi n^3. \tag{12}$$

We can relate n (quantum number of the electron in the solid) to the energy E using equation (9) to write the total number of states in terms of energy, $S(E)$. This is given by

$$S(E) = \frac{1}{3}\pi \left(8 m_e E\right)^{\frac{3}{2}} \frac{L^3}{h^3}. \tag{13}$$

Dividing by the volume of the cube will give total number of states per unit volume, $S_V(E)$. The density of states is the differential of the total number of states, so that $g(E)$ is given by

$$g(E) = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{\frac{3}{2}} \sqrt{E}. \tag{14}$$

Equation (14) gives the density of states (DOS) in a solid with a uniform potential. At the bottom of the band, which is normally chosen as the reference so energy is set to 0, and hence DOS is zero. As the energy increases $g(E)$ also increases. The functional form is shown schematically in Figure 22. $g(E)$ represents the density of available states. It does not provide information whether those states are occupied or not. The occupation is given by the Fermi function and is usually a function of temperature.

5.1.1 An example of density of states: silver

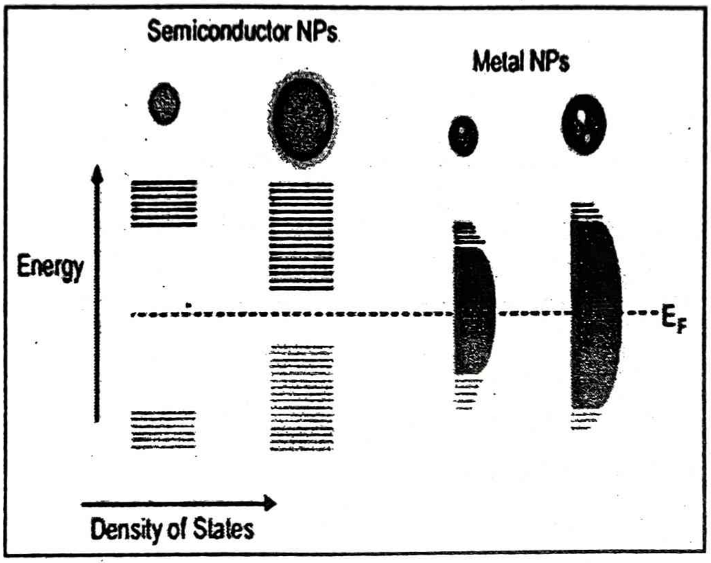

Figure 22: Density of states and location of Fermi level (E_F) for semiconductor and metal nanocrystals.

Consider an example to calculate the density of states in a metal, silver (Ag). Ag is a free electron metal, electrons in the outer shell are delocalized and are free to move in the material. Hence, valence electrons in Ag can be treated as electrons in an uniform potential. The atomic weight of Ag is 107.9 $gmol^{-1}$ and the density (ρ) is 10.5 gcm^{-3}. Hence the number of atoms per unit volume (n_V) can be calculated

$$n_V = \frac{\rho N_A}{At.\ wt}. \tag{15}$$

where N_A is Avogadros number. This gives n_V to be 5.85×10^{22} $atomscm^{-3}$. The Fermi energy (E_F) of Ag is at 5.5 eV . This is with reference to the bottom of the valence band (taken as zero). So the density of states, at the Fermi energy, for Ag can be calculated using equation (14) is given by

$$g(E) = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{\frac{3}{2}}\sqrt{E_F}. \tag{16}$$

where E_F is 5.5 eV. This gives a number 9.95×10^{46} $m^{-3}J^{-1}$ or converting the units 1.59×10^{22} $cm^{-3}eV^{-1}$. This is of the same order of magnitude as the number of atoms per unit volume.

Close to the bottom of the band the density of states is still a substantial quantity. Consider an energy $K_B\,T$ above the bottom of the band. At room temperature this energy is approximately 25 meV. Using equation (14), the density of states is $1.09 \times 10^{21}\ cm^{-3}eV^{-1}$ which is still a substantial fraction of the number of atoms.

In order to calculate the total number of electrons in the band, equation (14) has to be multiplied by the Fermi function $f(E) = \frac{1}{e^{\frac{E-E_F}{K_BT}}+1}$ and then be integrated from the bottom of the band to E_F. The occupation probability, $f(E)$ is 1. Then the number of electrons is given by (14) is given by

$$N(E) = \int_0^{E_F} g(E)\,dE = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{\frac{3}{2}}\frac{2}{3}E_F\sqrt{E_F} \tag{17}$$

The calculated value of $n(E)$ is $5.08 \times 10^{22}cm^{-3}$ which is very close to the number of atoms per cm^{-3}. Since each atom contributes one electron in Ag this is also the number of electrons and they fill all the states below E_F . Thus, a simple model of a solid with a uniform potential matches closely with reality. In silver, E_F is in the middle of the band so that there are empty available states for the electrons to occupy. When an electric field is applied, electrons travel opposite to this field and they can occupy these empty states. This makes Ag a very good conductor of electricity.

5.2 Density of States in a 2D uniform solid material

The density of states function will change upon changing the dimensionality of the solid. Consider the case of a 2D solid with a uniform potential. There are 2 quantum numbers, n_1 and n_2, which are related to the energy, similar to equation (9)

$$E = \frac{h^2}{8m_eL^2}\left(n_1^2 + n_2^2\right) = \frac{h^2n^2}{8m_eL^2}. \tag{18}$$

For a 2D case, n, represents the radius of a circle, shown in figure 4, and only the first quadrant can be considered since the quantum numbers should be positive. It is possible to calculate the density of states per unit area, $S_{area}(n)$, including spin

$$S_{area}(n) = \frac{\pi n^2}{2}. \tag{19}$$

Using equation (18) it is possible to calculate the DOS in terms of energy. Then $S_{area}(E)$ is given by

$$S_{area}(n) = \frac{4\pi m_e}{h^2}E. \tag{20}$$

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Differentiating equation (20) gives the density of states in two dimensions

$$g(E) = \frac{4\pi m_e}{h^2}. \tag{21}$$

The density of states function is independent of energy, unlike 3D where $g(E)$ increases with energy. It is represented as a step function at different energy values and shown in Figure 23.

5.3 Density of States in a 1D uniform solid material

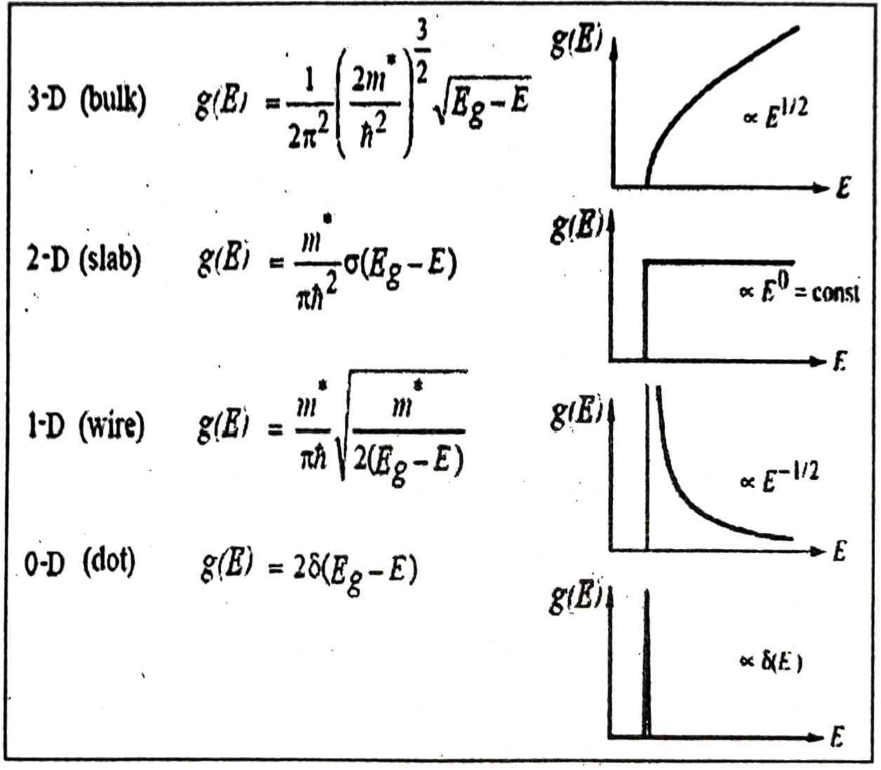
3-D (bulk)
$g(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E_g - E}$
2-D (slab)
$g(E) = \frac{m^*}{\pi\hbar^2}\sigma(E_g - E)$
1-D (wire)
$g(E) = \frac{m^*}{\pi\hbar}\sqrt{\frac{m^*}{2(E_g - E)}}$
0-D (dot)
$g(E) = 2\delta(E_g - E)$
$g(E)$
E
$\propto E^{1/2}$
$\propto E^0 = \mathrm{const}$
$\propto E^{-1/2}$
$\propto \delta(E)$

Figure 23: Comparison of density of states in different states.

The calculation for a 1D solid is similar to the earlier calculations except that there is only one quantum number and spatially it is represented on a line (instead of circle in 2D and sphere in 3D). The total number of states, per unit length, $S_{line}(n)$, is just $2n$ and this is related to energy E by the following equation

$$n = \sqrt{\frac{8m_e}{h^2}E}. \tag{22}$$

The density of states is given by

$$g(E) = \sqrt{\frac{8m_e}{h^2}}\frac{1}{\sqrt{E}}. \tag{23}$$

In a 1D solid the density of states decreases with energy.

For a zero dimensional solid, energy states are only discrete. Solids with two, one, and zero dimensionality can be obtained by reducing the length in one or more dimensions. A thin film is an example of a two dimensional solid (or a single or bilayer of graphene), while a quantum wire is a one dimensional solid. A quantum dot is a zero dimensional solid. The density of states and hence the electronic properties of these materials are different from a bulk solid. The DOS for solids at different dimensions are shown in Figure 23 as a function of energy.

6 Size effects in nanosystems

Nanoparticles are very small in size. They generally contain just a few atoms to a few thousand atoms. On the contrary, the bulk materials contain many billions of atoms. This difference in number of atoms causes nanomaterials to behave differently than their bulk counterparts. As material size decreases into the nanosize regime, novel properties arise that are different from their molecular and bulk counterparts. Due to the size and shape effects in this regime, a nanoparticle's morphology has a profound effect on its properties. This chapter addresses the effect of dimensionality on the optical, electronic, chemical, and physical assets of various nanomaterials and how physical and chemical relationships can be exploited to improve their properties. Delving into the nuances of the different sizes, shapes, and compositions gives one an appreciation of the potential that nanomaterials have to improve upon today's technologies. As scientists learn to fabricate increasingly more complex nanomaterials, new opportunities develop every day. A detailed discussion on the effect of morphology and nanometric dimensions on materials' physico-chemical properties,which lead to novel applications have been discussed below.

The design and controlled fabrication of colloidal materials with functional properties has flourished over the last few decades. The beauty and distinctiveness of nanoscale materials is rooted in their unique properties that emerge at the 1-100 nm scale. In this transitional regime, a material's physical, chemical, and biological properties may differ in fundamental ways from the properties of both bulk matter and the constituent atoms or molecules.

For decades, a staggering amount of research has focused on the creation of new nanomaterials and the elucidation of their unique property-structure correlations. Theoretical understanding of the mechanistic principles that govern the novel properties of the nanomaterials have also been studied extensively. Highly reliable bottom-up and top-down synthetic routes that produce increasingly complex nanomaterials with highly ordered and complex geometries have been developed. Complications in scaling up and uniformity that have hampered widespread application of nanomaterials in the early developments have been addressed to some extent. High throughput fabrication procedures amenable to scaling up for industrial scale implementation have been reported for many classes of nanoparticles.

6.1 How nanoparticles react with other elements

One aspect of how nanosized particles act differently is how they behave in chemical reactions. One of the most interesting examples of this involves gold.

Gold is considered an inert material in that it does not corrode or tarnish. Normally, gold would be a silly material to use as a catalyst for chemical reactions because it does not do much.

However, break gold down to nanosize (approximately 5 nanometers) and it can act as a catalyst that can do things like oxidizing carbon monoxide.

This transformation works as follows. The smaller the nanoparticle, the larger the proportion of atoms at the surface, and the larger proportion of atoms at the corners of the crystal. While in the bulk form, each gold atom (except the small percentage of them at the surface) is surrounded by twelve other gold atoms; even the gold atoms at the surface have six adjacent gold atoms. In a gold nanoparticle a much larger percentage of gold atoms sit at the surface. In Figure 24, gold nanoparticles are shown.

Because gold forms crystalline shapes, gold atoms at the corners of the crystals are surrounded by fewer gold atoms than those in the surface of bulk gold. The exposed atoms at the corners of the crystal are more reactive than gold atoms in the bulk form, which allows the gold nanoparticles to catalyze reactions.

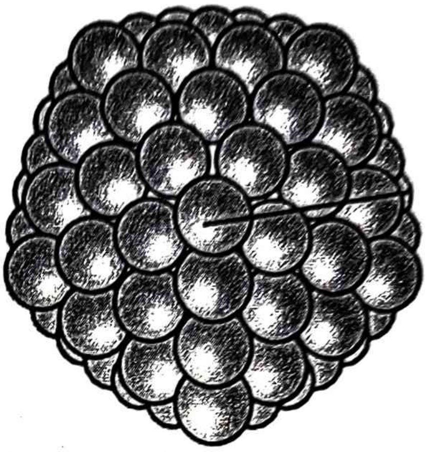

Figure 24: Gold nanoparticles.

6.2 How nanoparticles change color

Colloidal gold has been used by artists for centuries because of the nanoparticles interactions with visible light. Gold nanoparticles absorb and scatter light resulting in colors ranging from vibrant reds to blues to black and finally to clear and colorless, depending on particle size, shape, local refractive index, and aggregation state. These colors occur because of a phenomenon called Localized Surface Plasmon Resonance (LSPR), in which conduction electrons on the surface of the nanoparticle oscillate in resonance with incident light.

When gold is nanosized, it has some surprising properties. For example, nanogold can look red, orange, or even blue. The color depends on the size and shape of the nanoparticles and the distance between them. The different colors of nanogold come from a phenomenon called surface plasmon resonance. When light shines on the surface of a metal, it creates a surface plasmon, which is a group of electrons moving back and forth in sync across the surface of the metal. The electrons slosh back and forth on the metal surface, similar to the way waves of water move in a pond. When the electrons are moving at the same frequency as the light, the plasmon is said to be in resonance. When they are in resonance, the electrons absorb and scatter light, producing the colors. Nanoparticles of gold resonate at frequencies within the visible spectrum of light. Smaller nanogold particles absorb and resonate with purple, blue, green, and yellow wavelengths of light, so they look red. Larger nanogold particles absorb and resonate with green, yellow, and red wavelengths of light, so they look blue.

It turns out that golds capability to catalyze reactions is not the only thing that changes at the nanoscale. Gold can actually change color depending on the size of the gold particles.

One of the characteristics of metals is that they are shiny because light reflects off their surfaces. This reflectivity has to do with electron clouds at the surface of metals. Because photons of light cannot get through these clouds and therefore are not absorbed by the electrons bound to atoms in metals, the photons are reflected back to our eyes and we see that shiny bling quality.

In bulk form, gold reflects light. At the nanoscale, the electron cloud at the surface of a gold nanoparticle resonates with different wavelengths of light depending upon their frequency. Depending on the size of the nanoparticle, the electron cloud will be in resonance with a particular wavelength of light and absorb that wavelength.

A nanoparticle of about 90 *nm* in size will absorb colors on the red and yellow end of the color spectrum, making the nanoparticle appear blue-green. A smaller-sized particle, about 30 *nm* in size, absorbs blues and greens, resulting in a red appearance.

6.3 How nanoparticles melt at lower temperatures

Another characteristic that varies at the nanolevel is the temperature at which a material melts. In bulk form, a material, such as gold, has a certain melting temperature regardless of whether a small ring or a bar of gold is melted. However, at the nanoscale, melting temperatures begin to vary by as much as hundreds of degrees.

This difference in melting temperature again relates to the number of atoms on the surface and corners of gold nanoparticles. With a greater number of atoms exposed, heat can break down the bond between them and surrounding atoms at a lower temperature. The smaller the particle, the lower its melting point.

6.4 Size Effects on the Optical Properties in Nanosystems

A property describes how a material acts under certain conditions. The physical properties include optical (color and transparency), electrical (conductivity), physical (hardness, melting point) and chemical (reactivity, reaction rates). Properties are generally measured by looking at large (10^{23}) aggregations of atoms or molecules.

Besides these above stated ones, thermal and magnetic properties of materials also become size-dependent. Each one of these is described in detail below.

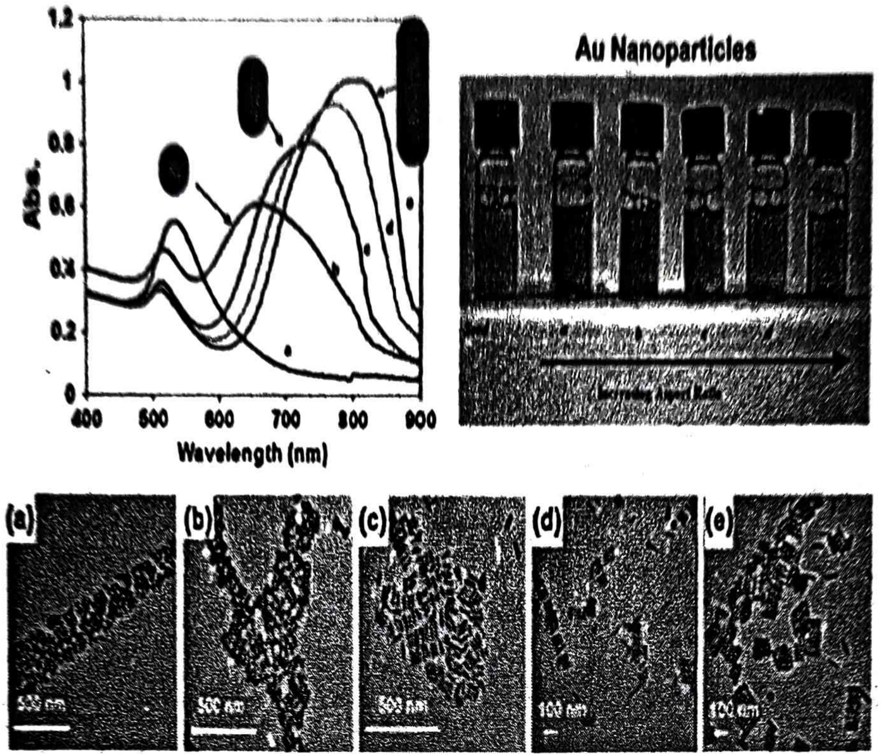

Figure 27: Shape dependence of the optical properties of gold nanostructures. Transmission electron micrographs (top), optical spectra (left), and photographs of (right) aqueous solutions of gold nanorods of various aspect ratios. Seed sample: aspect ratio 1; sample a: aspect ratio -1.4; sample b: aspect ratio -2; sample c: aspect ratio -3; sample d: aspect ratio -3.50; sample e: aspect ratio -4.4. Scale bars 500 nm for (a, b, c), and 100 nm for (d, e).

ble for their light absorption properties. Among many properties displayed by gold nanoparticles, one of the most notable is their ability to absorb and scatter light in the visible region of the electromagnetic spectrum as displayed in Figure 27.

The particles are so small that electrons are not free to move about as in bulk gold. Because this movement is restricted, the particles react differently with light.

Another comparison is made between large and nanosized zinc oxide particles, particles typically found in sunscreen. It shows how visible light and ultraviolet ray interacts with matter to allow us to see objects as having different colors and opacities. Generally large ZnO particles block UV light, scatter visible light and appear white whereas, nanosized ZnO particles block UV light, appear clear and are so small with respect to visible light that that they do not scatter visible light at all.

Nanoparticle shape dictates how sensitive the shift in the plasmon band is to changes in refractive index at the surface, which can be exploited to detect the presence of most inorganic, organic and biological molecules and surface synthesis, catalysis and molecular binding events. These asymmetric properties can lead to the creation of more sensitive sensors, faster electronics, more efficient energy storage devices and better catalysts. For intracellular delivery and imaging applications, the kinetics of cellular uptake and the effect of nanoparticles on cellular functions is dependent on nanoparticle shape.

7.6 Quantum Confinement

The quantum confinement (QC) effect is observed when the size of the particle is too small to be comparable to the de Broglie wavelength of the electron.To understand this effect we break the words like quantum and confinement. The word confinement means to confine the motion of randomly moving electron to restrict its motion. The consequence of this confinement in space is the quantization of their energy and momentum. In this case they are subjected to principles of the quantum mechanical motion rather than classical mechanics. So as the size of a particle decreases till we a reach a nanoscale the decrease in confining dimension makes the energy levels discrete and this increases or widens up the band gap and ultimately the band gap energy also increases. Thus, in nanocrystals, the electron energy levels are not continuous in the bulk but are discrete (finite density of states) and quantum reflects the atomic realm of particles. Nanocrystals are also referred to Quantum dots. If the size of the quantum dot is smaller than that of the Bohr radius then confinement occurs leading to a transition from continuous to discrete energy levels.

In the case of semiconductors, this QC simply means that the band gap, starting from the bulk value, increases as the size of the nanocrystal decreases. In the bulk solids, the energy levels are closely spaced, and thus form quasi-continuous bands. At nanoscale, the energy-level separation increases and discrete energy levels are observed, as shown in Figure 28. Calculations on different systems show that QCEs are observable at sizes $< 10\ nm$ for most of the nanomaterials. The onset of QC depends on a number of parameters, such as the dielectric constant of the semiconductor and effective masses of the charge carriers.

The length scale corresponds to the regime of quantum confinement ranges from 1 to 25 nm for typical semiconductor groups of IV, III-V and II-VI. In which the spatial extent of the electronic wave function is comparable with the particle size. As a result of these geometrical constraints, electrons feel the presence of the particle boundaries and respond to changes in particle size by adjusting their energy. Quantization effects become most important when the particle dimension of a semiconductor near to and below the bulk semiconductor Bohr exciton radius which makes materials properties size dependent. When the materials are so small, their electronic and optical properties deviate substantially from those of bulk materials. A particle behaves as if it were free when the confining dimension is large compared to the wavelength of the particle. During this state, the band gap remains at its original energy due to the continuous energy state. However, as the confining dimension decreases and reaches a certain limit, typically in nanoscale, the energy spectrum turns discrete. As a result, the band gap of the nanostructures becomes size and shape dependent. This ultimately results in a blue shift in optical illumination as the size and shape of the particles decreases.

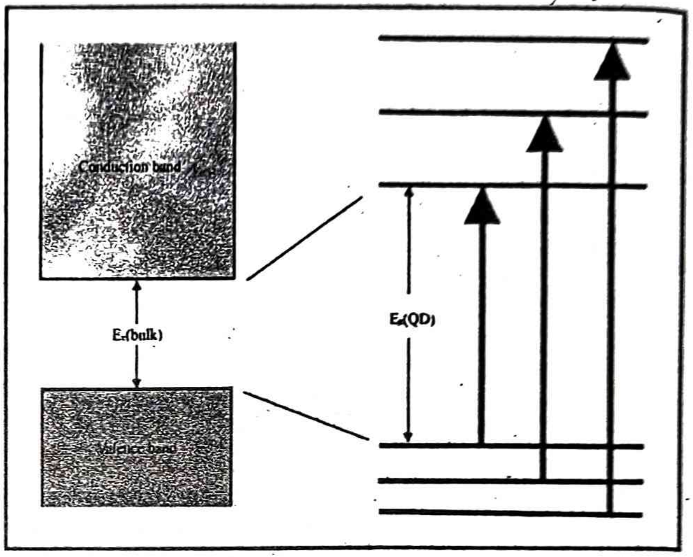

Figure 28: A schematic view of discrete energy levels of a semiconductor quantum dot.

Length scale plays a major role to determine the condition of applicability of quantum conditions in a system. This ultimately characterizes the quantum confinement in nanosystems. Such natural length scale is set by exciton Bohr radius. An exciton is the bound electron-hole pair in a semiconductor. In fact, the exciton Bohr radius $R_{exciton}$ is the distance between electron and hole in this pair. Replacing the mass of electron and hole by their reduced masses, the reduced mass of exciton is

$$m_{exciton} = \frac{m_e m_h}{m_e + m_h} = \frac{(0.067m_0)\times(0.45m_0)}{0.067m_0+0.45m_0} = 0.058m_0,$$

where $m_0 = 9.1 \times 10^{-31}\ kg$. $R_{exciton}$ is obtained as

✓ $$R_{exciton} = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{m_{exciton}e^2}.$$

This $R_{exciton}$ is the natural length scale and is compared to determine the condition for quantum confinement in a system. Objects with dimension shorter than $R_{exciton}$ will exhibit quantum confinement and manifest drastically different physical properties as compared to their bulk counterparts.

GaAs is a very useful compound semiconductor. The exciton Bohr radius $R_{exciton}$ for this semiconductor can be calculated in the following way:

$$R_{exciton} = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{m_{exciton}e^2} = \frac{4\times3.14\times8.85\times10^{-12}\times12.4\times\left(1.054\times10^{-34}\right)^2}{0.058\times9.1\times10^{-31}\times(1.6\times10^{-19})^2} = 11.3\ nm.$$ ✓

Here the dielectric constant $\epsilon_r = 12.4$ for $GaAs$ has been used. Thus, the characteristic length in $GaAs$ is 11.3 nm. If a $GaAs$ structure is made with dimension comparable to or smaller than 11.3 nm, its properties will be quite different from those of bulk $GaAs$ and quantum confinement can be observed in this structure.

Similar calculation for $CdSe$ shows that $R_{exciton}$ is 4.97 nm = 49.7 $\AA$. The required values of the parameters required for this calculation are: effective mass of electron = $m_e = 0.13m_0$,

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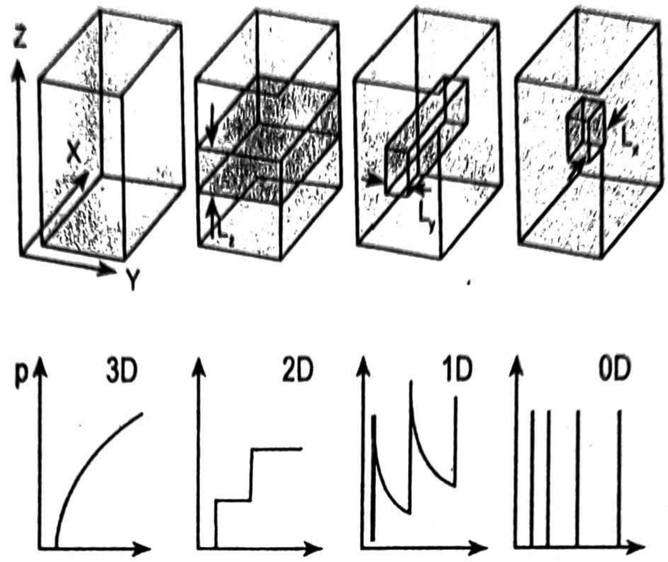

Figure 29: Schematics of density of states as a function of energy in bulk, quantum wells, quantum wires, and quantum dots.

effective mass of hole $m_h = 0.45m_0$ and the dielectric constant of $CdSe$ is $\epsilon_r = 9.4$. Below this length scale, the electron in the conduction band and hole in the valenee band in such semiconductor nanocrystals are confined due to quantum size effects. This quantum confinement also takes into account the aspect of the electronic structure of the nanoparticles that depends critically on the size of the particles. An electron behaves as if it were free when the confining dimension (by the boundary of the particle) is large compared to the de Broglie wavelength of the electron, and its energy spectrum is (quasi-) continuous. However, as the confining dimension decreases and reaches a certain limit, typically in the nanoscale, the energy spectrum turns to discrete. This is schematically shown in Figure 29.

In metals and semiconductors the electronic wave functions of conduction electrons are delocalized over the entire particle. These electrons can, therefore, be described qualitatively as particles in a "box". Thus the densities of states and the energies of the particles depend crucially on the size of the "box" which leads to some extent to a smooth size dependence. For example, ionization energies and electron affinities are tuned between the atomic values and the work function of the bulk material by variation of the cluster size. However, there are also discontinuities which are due to filled shell structures leading e.g. to extra stability of such clusters (pseudo-atoms).

The variation of nanoparticle size generates novel properties that can hardly be seen in the bulk, such as the conduction-insulator and nonmagnetic-magnetic transition of noble metals (e.g. Au at 2-3nm) at the nanoscale. We know that one electron energy level of atoms is split into two levels, when a two-atoms molecule is formed. With an increase in the number of atoms in the nanoparticle, the energy level continues to split and finally, merge into quasi-continuous band structure in the bulk solid. However, for small particles with dimension in the nanometer regime, the electron states are not continuous but discrete, due to the confinement of the electron wave function.

The quantum dot is a an assembly of atoms of specific material that has few nanometer dimensions. It is termed as a virtual atom or artificial atoms.Because of this microscopic size the electrons are confined inside the dot. This is the same for the electrons in an atom they are confined and localized in the atomic space.In order to obtain the possible energy levels in the atom or in the dot because of the space confinement one has to use quantum mechanical laws. That is one has to solve the Schrodinger equation with relevant boundary condition.The motion of electrons in the confined space can be modeled by the motion of a particle in a potential well with infinite walls.

While the atom is modeled by one well with infinite wall with size of the atom, the electrons in the quantum dot can be modeled by a potential well with infinite walls with the minimum energy level is that of the conduction band. Since we are interested in the confinement in the conduction band. Like wise we are interested in the holes in the valence band therefore, there will be an inverted well for the holes in the valence band. So, the picture is now is that we have electrons confined in the conduction band and holes in the valence band. If there is no confinement as in big crystal, there will be no confinement and the electrons in the conduction band will occupy the bottom of the conduction band and the holes will reside at the top of the valence band.

When we solve Schrodinger equation in potential well with infinite wall we find that the electrons will have only discrete energy levels in the valence band and so does the holes in the valence band. The energy level diagram in the conduction band will be similar to that of an atom and so the energy levels

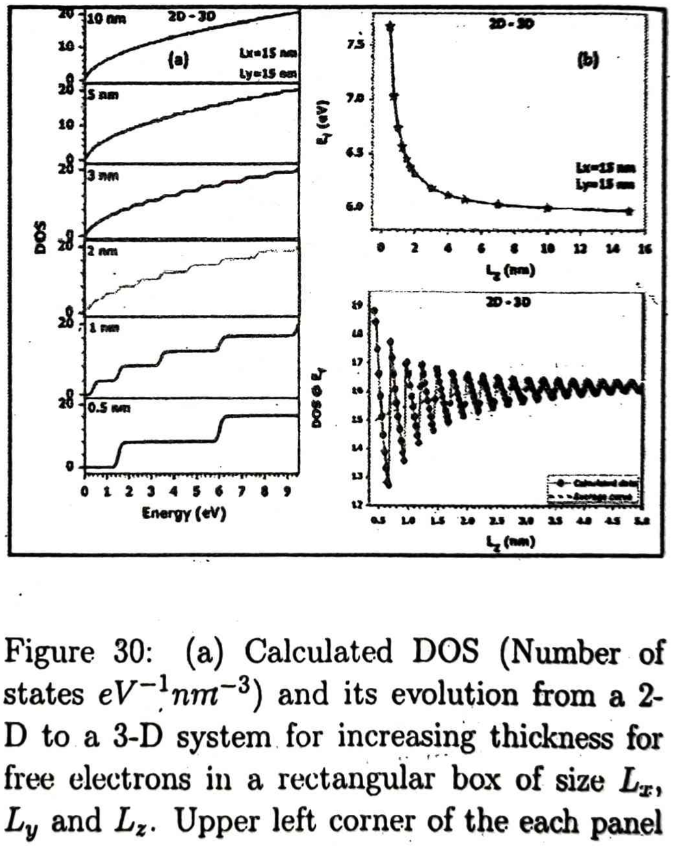

Figure 30: (a) Calculated DOS (Number of states $eV^{-1}nm^{-3}$) and its evolution from a 2-D to a 3-D system for increasing thickness for free electrons in a rectangular box of size L_x, L_y and L_z. Upper left corner of the each panel shows the thickness (L_z) and the lateral dimensions ($L_x = L_y = L$) are fixed at 15 nm for each case. (b) Fermi energies and (c) DOS at the Fermi energy are plotted for the structure evolving from 2D to 3D.

Table 2: Classification of quantum confinement structures.

Serial No	*Structure*	Quantum confinement	Number of free dimension
1	Bulk	0	3
2	Quantum well/superlattices	1	2
3	Quantum wire	2	1
4	Quantum ot/Nanocrystals	3	0

of the holes in the valence band will have also discrete energy levels.

When the particle size approaches Bohr exciton radius, the quantum confinement effect causes increasing of the excitonic transition energy and blue shift in the absorption and luminescence band gap energy. For example, 4.8 nm diameter $PbSe$ NCs show an effective band gap of approximately 0.82 eV, exhibiting a strong confinement induced blue shift of $> 500\ meV$ compared to the bulk $PbSe$ band gap of 0.28 eV (the Bohr exciton radius in PbSe is 46 nm).

In QDs, the charge carriers are confined in all three dimensions which the electrons exhibit a discrete atomic-like energy spectrum. Quantum wires are formed when two dimensions of the system are confined. In quantum well, charge carriers (electrons and holes) are confined to move in a plane and are free to move in a two-dimensional. Also the energy level of one of the quantum numbers changes from continuous to discrete. Such confinement dimensions in different systems are shown in Table 2. Compared with bulk semiconductors, the quantum well has a higher density of electronic states near the edges of the conduction and valence bands, and therefore a higher concentration of carriers can contribute to the band-edge emission. As more number of the dimension is confined, more discrete energy levels can be found, in other words, carrier movement is strongly confined in a given dimension. It should be mentioned here that self-assembled nanostructures basically do not show any blue shift, but the core/shell nanostructures exhibit a significant blue shift, leading to the QCEs.

The major part of this theory is the behavior of the exciton ensembles more like an atom as its surrounding space shortens. A rather well approximation of exciton behavior is the 3D model of a particle in-a-box. The solution to this problem provides a sole mathematical connection between energy states and the dimension of space. It is obvious that if volume or the dimensions of the available space decreases, the energy of the states increase. The schematic band diagram shows the change in electron energy level and band gap between a nanomaterial and its bulk state. The relationship between energy level and dimension spacing can be described by

$$\Psi_{n_x,n_y,n_z} = \sqrt{\frac{8}{L_x L_y L_z}}\ sin\left(\frac{n_x \pi x}{L_x}\right) sin\left(\frac{n_y \pi y}{L_y}\right) sin\left(\frac{n_z \pi z}{L_z}\right), \tag{24}$$

where

$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2m}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right]. \tag{25}$$

This is the energy level in the quantum level of materials/atoms. Due to the 1D confinement, the electron energy levels can be found from the solution of the Schrdinger equation for an infinitely deep potential well with the form

where

$$E_n = \frac{\pi^2\hbar^2 n^2}{2\mu L^2}. \quad n = 1, 2, 3, ... \tag{26}$$

where μ is the effective mass of the electron and the dependence of the energy levels on L^2 is the quantum size effect. The dispersion relation for the conduction band can be as (for confinement in the Z-direction)

$$E(k) = E_C + E_{n_z} + \frac{\hbar^2({k_x}^2 + {k_y}^2)}{2\mu} \tag{27}$$

where E_{n_z} is given by Eq. (26). For the conduction band, the density of states per unit area in a 2D QW system in the sub-bands can be expressed as (for energies greater than $E_C + E_{n_z}$) $g(E) = \frac{u^2}{(\pi\hbar)^2}$. Thus, for each quantum number n_z, the density of states is constant and the overall density of states is the sum of these for all values of n_z, which results in a staircase-type distribution with a step height given by $g(E)$. In a 1D QW system, the carriers are confined in two directions (Z and X), and the dispersion relation for the conduction band can be written as

$$E(k) = E_C + E_{n_z} + E_{n_x} + E_{n_x}. \tag{28}$$

In this case, the density of states (DOS) is described by a set of discrete functions as shown in Figure 30. Thus, QDs are generally referred to as artificial atoms due to the similar discrete energy-level structures. It is noteworthy to mention that the density of states in the valence band has a similar distribution to that in the conduction band state.

7.1 Application of *Schrödinger*'s equation

See the notes :
all applications

According to de Broglie hypothesis, a particle behaves like a wave under suitable conditions. The Heisenberg's uncertainty principle states that when the momentum of a particle is well defined, the associated de Broglie wave can be of infinite extent. Therefore, a free particle of mass 'm' moving with a well defined momentum in the positive can be described by an infinite plane wave

$$\Psi(x,t) = A_0\, exp\left[i(kx - \omega t)\right] \tag{29}$$

where the wave vector $k = \frac{2\pi}{\lambda}$, ω is the angular frequency and A_0 is the amplitude. It is known that in case of electromagnetic waves, the electromagnetic field varies in space and time. In case of sound waves, it is the pressure that varies in space and time. Thus, we need a quantity to describe wave motion which will vary in space and time. This variable quantity is called the wave function $\Psi(x,t)$. It is generally used to express a matter wave associated with a moving particle. It has the largest value in the regions where the particle is likely to be found and small in the region where it is less likely to be found. That is, the wave function of a particle in conformity with the uncertainty principle must be localized in a small region around it. The wave function of the matter wave which is confined to a small region is known as the wave packet or wave group. This is shown in Figure 31.

Mathematically, a wave packet is constructed by applying the principle of superposition to an assembly of infinite number of plane waves with different values of wave vector $\vec{k}$. These plane waves are represented by equation (29). This wave packet is given by

$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k)\, exp\left[i(kx - \omega(k)t)\right] dk. \tag{30}$$

Thus, for a localized particle, the superposition principle provides a wave packet traveling without change in shape. This demands that $A(k)$ will be zero everywhere except for a small region for the values of k lying in a certain range. In order to find the dynamics of a system, we have to set up an equation of motion for $\Psi(x,t)$. This equation of motion was formulated by Erwin *Schrödinger* in 1926. This equation is a fundamental one in quantum mechanics as Newton's equation in classical physics.

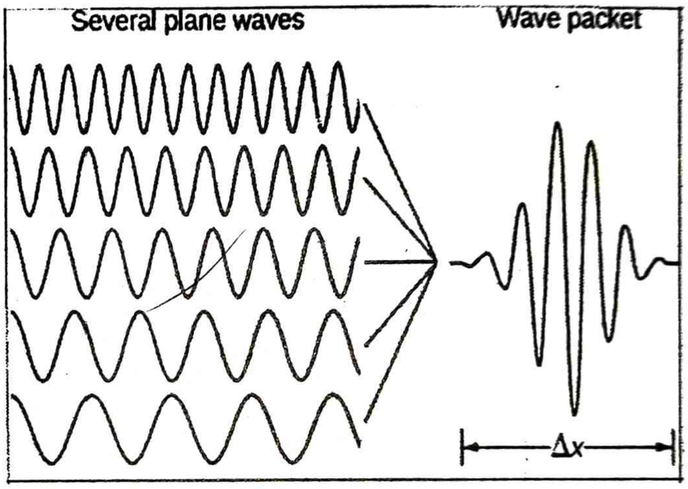

Figure 31: A wave packet representing free particle.

7.2 *Schrödinger*'s equation from wave packet

We consider a free particle of mass 'm' moving with velocity v_x and momentum p_x. As the particle is free, it is not subjected to any potential ($V = 0$) and its total energy E is equal to the kinetic energy i.e. $E = \frac{p_x^2}{2m}$. Again we have, $p_x = \hbar k$ and $E = \hbar\omega$. Using these two expressions, over conventional methods involving chemical agents associated with environmental toxicity. Selection of solvent medium and selection of ecofriendly non-toxic reducing and stabilizing agents are the most important issues which must be considered in green synthesis of NPs.

To synthesize different types of nanomaterials in the form of cluster, colloids, rods, thin films, tubes, wires, etc. a large number of techniques are available in literature. Continuing attempts are being made to upgrade the existing conventional techniques to synthesize different types of materials and some new techniques are being developed. Since nanotechnology is an interdisciplinary subject, available methods such as chemical, physical, hybrid, biological are used by researchers in various fields to synthesize nanomaterials. For all each types, there are number of possibilities. The technique to be used depends upon the material of interest, type of nanostructure viz. 0-D, 1-D or 2-D material, size, quantity etc.

In this chapter, existing conventional techniques which are normally used to synthesize different types of nanomaterials are briefly described. Each technique is presented with detailed description of the experimental set-up, and their advantages and disadvantages.

1.1 What is synthesis?

Synthesis of nanoparticles refers to methods for creating nanoparticles. It is a process by which nanoparticles can be derived from larger molecules (top-down method), or synthesized by "bottom-up" methods. In this 'bottom-up' method, nucleation occurs and particles grow from fine molecular distributions in liquid or vapor phase. Synthesis also includes functionalization by conjugation to active molecules in biological systems.

Over the last few decades, strong technological development has enabled manipulation of synthesis of the nanomaterials with shaped-up properties to meet the needs of typical applications. One can actually tailor up the properties of low-dimensional materials by the methods of physical chemistry. There is always a way of how to control the size, shape, crystal structure, and surface formation to bring the materials to meet the requirement of any targeted application. Controlling of the dimensions of the nanoparticles is the challenging task for any modern research in nanotechnology.

1.2 Different processes of synthesis of nanomaterials

Nanoparticles can be synthesized using a variety of methods including physical, chemical, biological, and hybrid techniques. The production of nanoparticles through conventional physical and chemical methods results in toxic byproducts that are environmental hazards. Additionally, these particles cannot be used in medicine due to health-related issues, especially in clinical fields. Conventional methods can be used to produce nanoparticles in large quantities with defined sizes and shapes in a shorter period of time; however, these techniques are complicated, costly, inefficient, and outdated. In recent years, there has been growing interest in the synthesis of environmentally friendly nanoparticles that do not produce toxic waste products during the manufacturing process. This can only be achieved through benign synthesis procedures of a biological nature using biotechnological tools that are considered safe and ecologically sound for nanomaterial fabrication as an alternative to conventional physical and chemical methods. This has given rise to the concept of green technology or green nanobiotechnology. Various methods for synthesis of nanoparticles are shown in Figure 1.

1.3 Factors affecting the synthesis of nanomaterials

Synthesis procedures depend on the detailed investigations of the factors affecting the synthesis of various types of nanoparticles using green technology and their characterization. Therefore, this section is dedicated to highlight the factors influencing synthesis of nanoparticles using green technology and different techniques for characterization of nanoparticles. This will provide a better understanding of nanoparticles and improve their uses in modern technology.

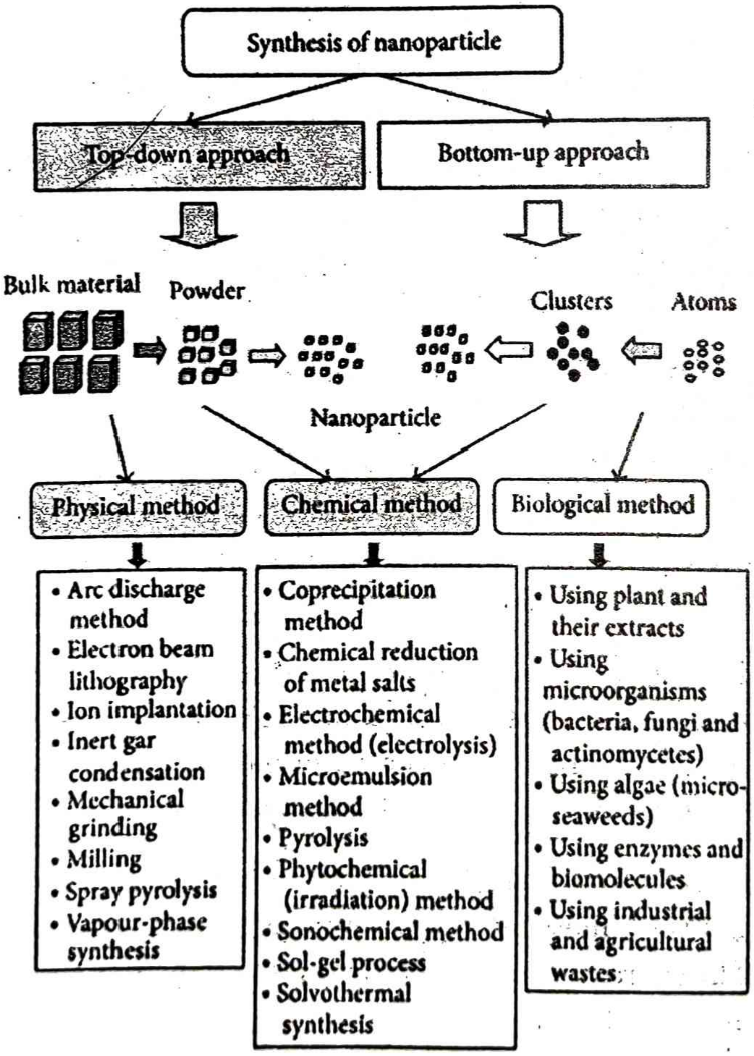

Figure 1: Various types of methods for synthesis of nanoparticles.

There are several factors which affect the synthesis, characterization, and application of nanoparticles. The nature of the synthesized nanoparticles depends on the type of the adsorbate and the activity of the catalysts used in the synthesis process. The dynamic nature of the synthesized nanoparticles changes with different types of symptoms with the change in time and environment. The important factors that affect the synthesis of nanoparticles include pH of the solution, temperature, concentration of the synthesis. Furthermore, the choice of method used to purify the synthesized nanoparticles can influence nanoparticle quantity and quality. In some cases, centrifugation is performed to separate the nanoparticles based on gravitational force. In other cases, chromatography techniques are used to separate nanoparticles according to differences between the mobile phase and stationary phase coefficients. Efficient separation of synthesized nanoparticles is achieved by one or more procedures, including the extraction of nanoparticles based on their solubility in two different miscible liquid phases (usually water and organic solvents) followed by electrophoresis or chromatography.

2 Synthesis of nanomaterials

Synthesis is the process of the production of a substance by the union of chemical elements, groups, or simpler compounds or by the degradation of a complex compound. There are various synthesis procedures of nanomaterials which can be broadly classified into three categories as follows:

Physical process: Physical synthesis procedures includes arc discharge method, electron beam lithography,mechanical grinding, inert gas condensation, ion implantation, ball milling, spray pyrolysis, vapor phase synthesis etc. These procedures are generally applicable at temperatures above 350^oC.

Chemical process: These are the simplest and most inexpensive methods for the synthesis of nanomaterials. Another advantage is that these processes are applicable at low temperatures and a nanosamples can be produced in a large scale. Sol gel process is the most popular chemical process for nano material synthesis. Moreover coprecipitation method, microemulsion method, electro chemical method, pyrolysis, irradiation, solvothermal, sonochemical etc. are some other chemical processes for nanomaterial synthesis.

Biological process: This type of synthesis process use micro organisms, plant extracts or DNA, virus, membrane etc. as templates for synthesis of nanomaterials. Advantage of biological process over chemical process is that the later one are more environment friendly.

Various processes for synthesis of nanomaterials using physical and chemical processes are shown in Figure 2.

2.1 Top down approach

In top-down approach, nanoscale objects are made by processing larger objects in size. Integrated circuit fabrication is an example for top down nanotechnology. Now it has been grown to the level of fabricating nanoelectromechanical systems (NEMS) where tiny mechanical components such as levers, springs and fluid channels along with electronic circuits are embedded to a tiny chip. The starting materials in these fabrications are relatively large structures such as silicon crystals. Lithography is the technology which has enabled making such tiny chips and there are many types of them such as photo, electron beam and ion beam lithography.

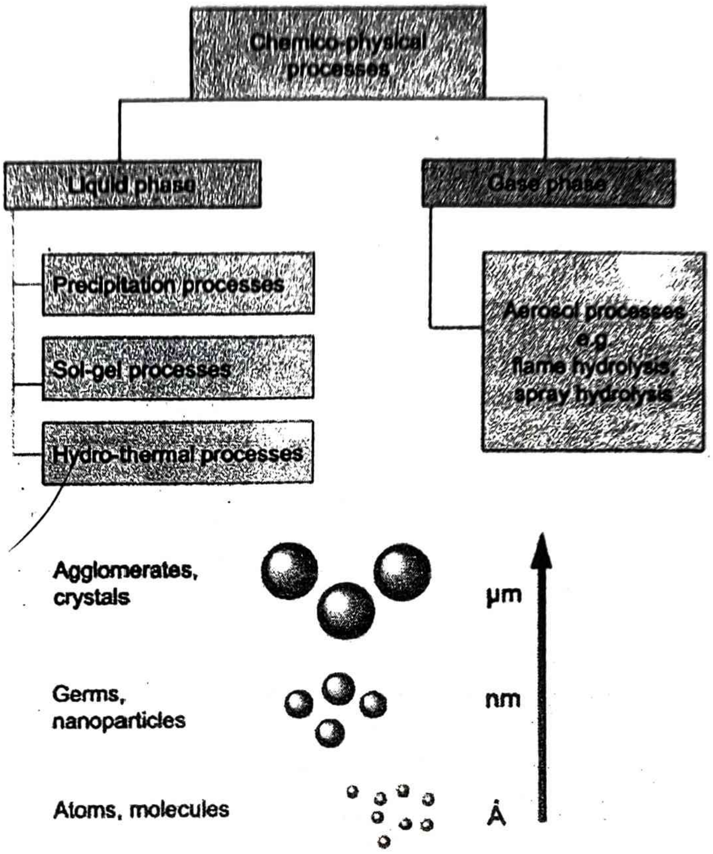

Figure 2: Chemo-physical processes in nanoparticle synthesis.

This procedure involves the reduction of size from a larger assembly of Nanostructure or bulk material. Basic principle of this approach is to break larger grain sizes of the bulk material into smaller one by the use of physical processes like crushing, milling or grinding. Top down approach includes one of the most popular method for synthesis - solid state reaction. However, there are some limitations of this approach. Uniformly shaped materials can not be prepared through this route. The biggest problem of this method is the imperfection of the surface structure of the as prepared sample. Such imperfection always have a significant impact on physical properties of nanomaterials. Moreover, the conventional top-down technique can cause significant crystallographic damage to the as prepared samples patterns. These methods are schematically shown in Figure 3.

In some applications larger scale materials are grinded to the nanometer scale to increase the surface area to volume aspect ratio for more reactivity. Nanogold, nanosilver and nanotitanium dioxide are such nanomaterials used in different applications. Carbon nanotube manufacturing process using graphite in an arc oven is another example for top-down approach nanotechnology.

2.1.1 Top-down technologies

The following technologies are included in top-down technology:

1. Mechanical grinding.
2. Metal vapor

5

3. Thermal breakdown.
4. Chemical breakdown.
5. Spontaneous chemisorption.

2.1.2 Disadvantages of top-down technologies

Though chemical purification is not required, this process suffers from several disadvantages. These are listed below:

1. size distribution of the particles is broad (10 – 100 nm).
2. shape or geometry of the particles vary.
3. control over the deposition parameters is difficult to achieve.
4. impurities, stresses, defects and imperfections are introduced.

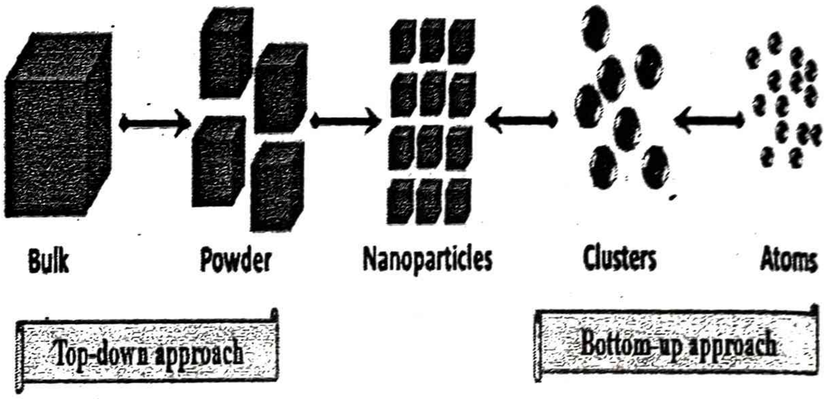

Figure 3: a) Top down and b) Bottom up approach.

2.2 Bottom up approach

Bottom-up approach in nanotechnology is making larger nanostructures from smaller building blocks such as atoms and molecules. Self assembly in which desired nanostructures are self assembled without any external manipulation. When the object size is getting smaller in nanofabrication, bottom-up approach is an increasingly important complement to top-down techniques.

This route refers to build up the nanostructure from the bottom which may be atom by atom or molecule by molecule or cluster by cluster. It is more frequently used for preparing most of the nanosized materials with the ability to generate a uniform size, shape and distribution.

It effectively covers chemical synthesis and precisely controls the reaction to inhibit further particle growth.

Bottom-up approach nanotechnology can be found from nature, where biological systems have exploited chemical forces to create structures for cells needed for life. Scientists and engineers perform research to imitate this quality of nature to produce small clusters of specific atoms, which can then self assemble into more complex structures. Manufacturing of carbon nanotubes using metal catalyzed polymerization method is a good example for bottom-up approach nanotechnology.

Molecular machines and manufacturing is a concept of bottom-up nanotechnology introduced by Eric Drexler in his book Engines of Creation in 1987. It has given early views of how can nanoscale mechanical systems be used to build complex molecular structures.

2.2.1 Bottom-up technologies

The following technologies are included in bottom-up technology:

1. Sol-gel.
2. Chemical reduction of salts.
3. Electrochemistry.
4. Solvothermal processing.
5. Template-directed.
6. Precipitation.
7. Microemulsion.

2.2.2 Disadvantages of bottom-up technologies

Though chemical purification is not required, this process suffers from several The disadvantages of the method are listed below:

1. Large scale production is difficult.
2. Chemical purification of nanoparticles is required.

2.3 Difference between top-down and bottom-up approach in nanotechnology

There are certain differences between top-down and bottom-up approaches for the synthesis off nanomaterials in nanotechnology. These are listed below:

1. Manufacturing process starts from larger structures and becomes smaller and smaller in top-down approach whereas starting building blocks are smaller than the final products in bottom-up approach.
2. Bottom-up manufacturing can produce structures with perfect surfaces and edges (not wrinkly and does not contain cavities etc.) though surfaces and edges resulted by top-down manufacturing are not perfect as they are wrinkly or containing cavities.
3. Bottom-up approach manufacturing technologies are newer than top-down manufacturing and expected to be an alternative for it in some applications (example: transistors).
4. Bottom-up approach products have a higher precision accuracy (more control over the material dimensions) and therefore can manufacture smaller structures compared to top-down approach.
5. In top-down approach there is a certain amount of wasted material as some parts are removed from the original structure contrast to bottom-up approach where no material part is removed.

3 Photolithography

Lithography is one of the most used techniques in top down approach. The word 'lithography' originates from a Greek word "litho" that means stone and "grapia" which means to write. So the word 'lithography' literally refers to writing on stone. The word photo means light and in case of photolithography, silicon wafers act as stone and patterns are written on its surface with the help of a light sensitive polymer called as a photoresist or resist. The entire process consists of a series of steps which establish the shape, dimensions and location of some parts of a bulk surface or of a thin film. The steps involved in the photolithography process are wafer cleaning; barrier layer formation; photoresist application; soft baking; mask alignment; exposure and development; and hard-baking.

Photolithography uses ultra-violet (UV) light to create patterns or shapes on a material. Therefore, this process is also referred to as optical lithography or UV lithography. Photolithography is a manufacturing process mainly used in IC (integrated circuit) designing in the semiconductor industry. With the miniaturization of IC chips and increased density of transistors, IC design can progress if and only if smaller areas on a silicon wafer surface can be patterned. This is primarily the function of lithography. Photolithography is used in research to make patterns with a high level of precision. It is also widely used in making of microfluidics devices, microelectronic circuits and microelectromechanical systems using photoresist films. This technique requires a source of UV light, photoresist material and mask.

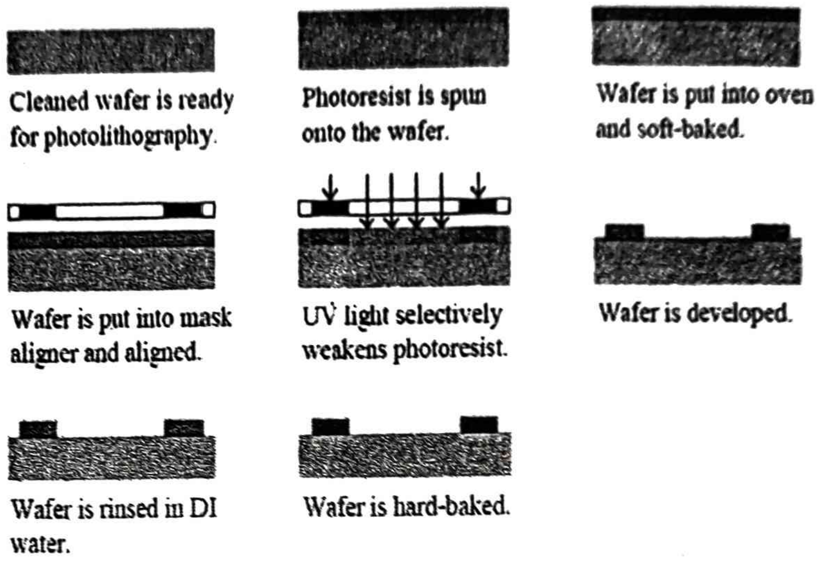
Cleaned wafer is ready for photolithography.
Photoresist is spun onto the wafer.
Wafer is put into oven and soft-baked.
Wafer is put into mask aligner and aligned.
UV light selectively weakens photoresist.
Wafer is developed.
Wafer is rinsed in DI water.
Wafer is hard-baked.

Figure 4: Steps involved in photolithogrphy.

The process utilizes the energy of light, such as ultraviolet light, to transfer 2D and 3D geometrical features through a mask onto the surface of a substrate/silicon wafer. The photomask contains the master image, which is transferred onto the wafer. The pattern transfer process consists of two parts: a photo-process, during which the desired pattern is transferred through a photo-mask onto a photosensitive film; and a chemical process which removes unwanted photosensitive material after exposure. Photo-masks pose technical and financial complications effecting quality and final cost of the manufactured silicon wafer. One technical complication of masked photolithography is alignment. Alignment of the photo-mask complicates the process during exposure. When the photo-mask is not perfectly aligned with the underlying layer, regions of the underlying layer may overlap forming what is known as disorder. The disordered wafer shows visible faults in its geometrical features. The slightest misalignment jeopardizes the uniform distribution of the electrical resistance. Mechanical shift errors may also occur during exposure of misaligned photo-mask. A financial complication effecting masked photolithography is the high cost of manufacturing photo-masks. The manufacturing cost of the photo-mask continues to rise as the market demand for complex shapes and high resolution patterns increases. The manufacturing cost depends on size of the mask and the complications of the patterns. It also depends on type of raw materials, fabrication process, and special expertise required in manufacturing the photo-mask. The manufacturing cost of the photo-mask accounts for 40% of the final products cost (however this number will decrease with increasing production volume of chips fabricated). The complication of using conventional photo-lithography directed the market to focus on alternative methods such as the mask-less photolithography technique. This innovative process has been introduced to the market as

Advantage :

1. It is a versatile method.
2. It is highly suitable for mass production.
3. This process is widely used for the fabrication of high density and large array size materials.
4. This process can be used to analyze the neutrophils which are an important part of the innate immune system. These could help study the reaction time and diagnostics to make devices that detects disease.
5. The photolithography is used extensively in integrated circuit patterning process.
6. It is also used in printing electronic board, nameplate, printer plate etc.

3.4 Disadvantages of photolithography

There are certain disadvantages of this procedure. These are listed below:

1. The disadvantages of using photolithography are that it is very expensive because of the cost of the machines.
2. This process needs for access to a clean room; or a room with dim lights that prevents UV radiation specifically for photolithography.
3. Another disadvantage is that the surface properties like specific chemical properties to adhere to adsorption cannot be controlled nor manipulate and has a rigid structure.
4. This procedure can only cut the material unidirectional; only vertically, and is unable to be cut horizontally.
5. Depending on the complexity of the experiment, it takes a long time to design and develop a prototype.
6. The materials used for this technique is not suitable for biological systems because it is unable to simulate a biological system.

These disadvantages are compensated by adding soft lithography techniques to the material.

4 Ball milling

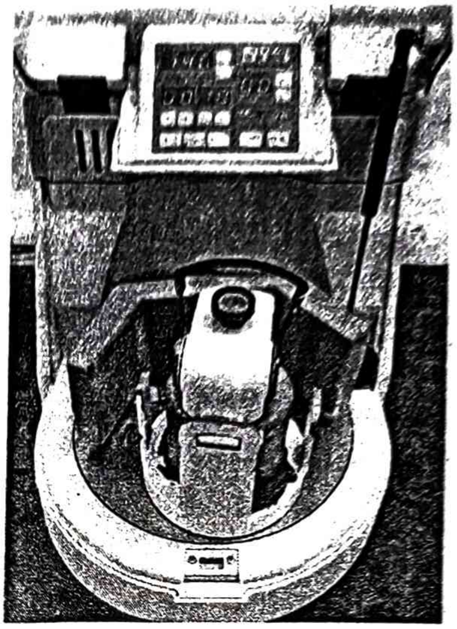

Figure 7: Diagram of a ball milling machine used in research laboratory.

Ball milling is a very popular physical method for synthesis of nanomaterials. It is an example of top down approach. An image of practical ball milling machine is shown in Figure 7. Ball milling is a mechanical technique widely used to grind powders into fine particles and blend materials. Being an environmentally-friendly, cost-effective technique, it has found wide application in industry all over the world. A ball mill is basically a grinder equipment used to reduce the particle size of active and excipient materials. It is also known as pebble mill or tumbling mill. The quality of dispersion is affected by the factors such as the milling time, rotational speed, size of balls and balls/dispersion amount ratio. Under certain processing conditions, the particles can be ground to as small as 100 nm. This technique has several advantages which include cost-effectiveness, reliability, ease of operation, reproducible results due to energy and speed control, applicability in wet and dry conditions on a wide range of materials. Examples of such materials are cellulose, chemicals, fibres, polymers, hydroxyapatite, metal oxides, pigments, and catalysts.

Depending on the material to be treated, different types of ball milling equipments are available. In particular, the ball mills are classified in two groups depending on their operation mode: direct and indirect milling. In the first case rollers or mechanical shafts directly act on the particles and transfer the kinetic energy. In the second case the kinetic energy is firstly transferred to the mill body and then to the grinding medium. These ball mills are the most widely used in the field of cellulose and they can be further divided into three groups: tumbler ball mills, vibratory mills and planetary mills. A tumbler mill consists of a cylinder partially filled with steel balls rotating about its longitudinal axis. In this type of instrument, the efficiency of the process mainly depends on the diameter of the mill. Larger diameters allow greater height of the fall and consequently a higher energy transmitted to the balls. In vibratory mills the vessel containing the sample and the grinding medium are shaken back and forth at high vibrational frequencies. Important factors, in this case, are the vibrational frequency, the amplitude of vibration and the mass of the milling medium. Finally, in a planetary mill the

A variant of the rotating (or tumbling) ball mill is the planetary ball mill. This variant imparts a higher degree of energy in an attempt to create finer or more homogeneous powder size distributions. Instead of relying on gravity to accelerate the balls, the mill chamber is placed off-center on a rotating platform. The mill chamber then rotates in the opposite direction to the rotating central platform. The net effect is that tumbling milling media are accelerated within the mill chamber, not by gravity, but by the centrifugal force created by the spinning central platform.

4.4 Advantage of ball milling

Ball milling method has several advantages of nanomaterial synthesis. These are listed below:

1. It produces very fine powder (particle size less than or equal to 10 microns).
2. It is suitable for milling toxic materials since it can be used in a completely enclosed form.
3. It has a wide application in nanomaterial synthesis.
4. It can be used for continuous operation.
5. It is used in milling highly abrasive materials.

4.5 Disadvantage of ball milling

In spite of several advantages of the method of ball milling for the synthesis of nanomaterials, this method suffers from several drawbacks as well. These are listed below:

1. Contamination of product may occur as a result of wear and tear which occurs principally from the balls and partially from the casing.
2. High machine noise level especially if the hollow cylinder is mode of metal, but much less if rubber is used.
3. Relatively long time of milling.
4. It is difficult to clean the machine after use.

5 Gas phase condensation

There are mainly three groups of synthesis methods for producing nanoparticles. The first group comprises the liquid-phase methods, which apply chemical reactions in solvents. The second group consists of methods, that are based on surface growth under vacuum conditions. Most of the synthesis methods of nanoparticles that come in the gas phase are based on homogeneous nucleation in the gas phase and subsequent condensation and coagulation.

Gas phase condensation methods have attracted huge interest over the past few decades. They can deliver a number of benefits over other synthesis methods. Gas phase condensation techniques are typically characterized by the ability to accurately control the process parameters to be able to tune the shape, size and chemical composition of the nanostructures. The most rudimentary gas phase condensation technique is the inert gas condensation which started its journey around 1930's. A similar method has been used in the manufacture of carbon black, an ink pigment, since ancient times. The technique employed now for the formation of nanopowders, in reality, differs from that used to produce carbon and lampblack primarily in the choice of atmospheric composition and pressure and in the use of a chemically reactive source. A number of significant nanostructures are fabricated through this process over the past few years. For example, CdS nanoparticles (16 nm) which are widely used in catalysis and optical devices have been synthesized in this method. Magnetic nanoparticles of Co (10 nm) have been also synthesized via this method. A schematic diagram of gas phase condensation is shown in Figure 10.

5.1 Basic principle of gas phase condensation

As the name suggests gas phase condensation uses evaporation of a metallic source in an inert gas atmosphere to form nanoparticles. In its basic from a metallic source which has to be made into nanostructured is used as a heating element inside a chamber. The chamber has to be previously evacuated to about 10^{-7} torr (1 mm of Hg) and backfilled with inert gas to a low pressure. The adjustment of pressure inside the vacuum chamber is a tricky job. The pressure has to be high enough to promote particle formation, but low enough to prevent their agglomeration.

On resistive heating, the metal vapor migrates from the hot source into the cooler inert gas by a combination of convective flow and diffusion. The evaporated metal atoms collide with the gas atoms within the chamber and loose kinetic energy and finally the metal atoms get condensed. Ultimately, the particles are collected for subsequent consolidation, usually by deposition on a cold surface.

After evaporation of the metal vapor, the liquid particles collide and coalesce in a controlled environment such that they can grow as per specification. As the liquid particles are further cooled under control, they become solid and prevent any further growth. In most of the cases of inert gas condensation technique, the substrate is cooled with liquid nitrogen to enhance the deposition efficiency. Particles collected in this manner are highly concentrated on the deposition substrate. While the particles deposited on the substrate have complex aggregate morphology, the structure tends to be classified in terms of the size of the crystallites that make up these larger structures.

At this stage the nanoparticles are very much reactive. To prevent agglomeration with any other materials the nano particles are coated with coping agent. Then scraping and compaction processes take place within the clean environment to ensure powder surface cleanliness (i.e., to reduce oxide formation) and to minimise problems associated with trapped gas.

In this process the parameters which can control the quality of shape and size of the nanomaterials are vapor concentration, temperature and pressure, physical properties (melting point) of the metal. Under same conditions metal with a high melting point produces smaller particles. Collection of fine sized nanopowder is another tricky job because the nano particles tend to suspend in the gas in constant Brownian motion and therefore not setteled by the action of gravity. Special filters are used and centrifugal sedimentatin are used to collect powder particles.

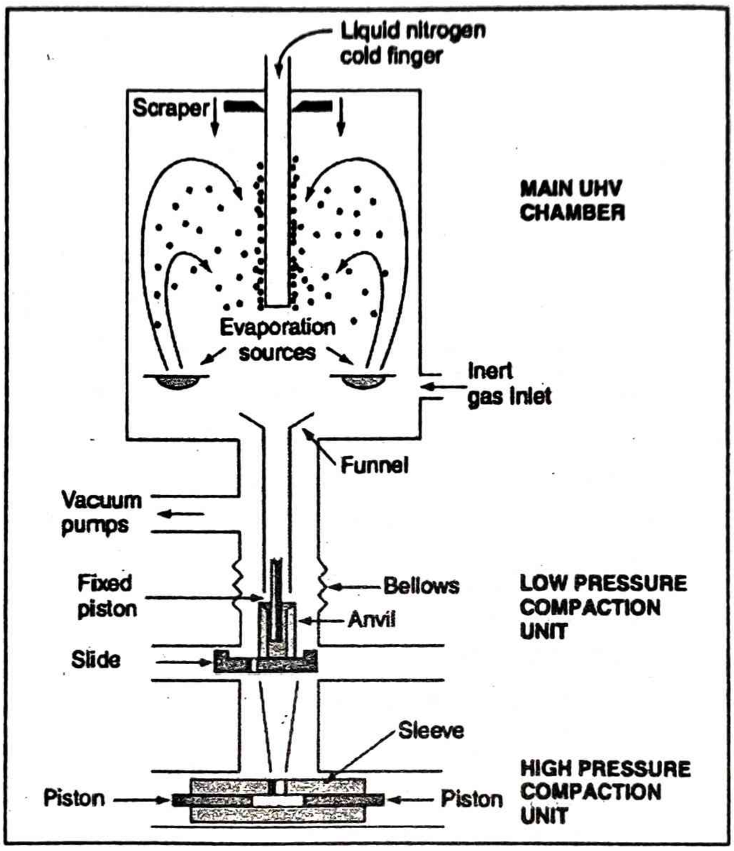

Figure 10: Schematic diagram of inert gas phase condensation.

5.2 Advantage of gas phase condensation

Gas phase condensation method has several advantages for the synthesis of nanomaterials. These are listed below:

1. The process is very old but it provides a good control over the shape and size of the final products.
2. It is a continuous process. Both thin films and nanopowder can be produced via this

method.

3. This process is ideally suited for the synthesis of metal nanoparticles.
4. It ensures highest purity relative to liquid phase or solid phase synthesis processes.
5. Multi component (nanoparticles that contain two or more dissimilar elements, and they have more beneficial properties) nanomaterials can be fabricated by this process with better performance.
6. It can be used for large scale production i.e. larger quantity of the materials can be produced in this process.

5.3 Disadvantage of gas phase condensation

In spite of several advantages of the method of gas phase condensation for the synthesis of nanomaterials, it also suffers from some drawbacks. These are listed below:

1. The process is indeed very slow.
2. Besides, the aggregation of particles presents a problem in this process.
3. Adjustment of pressure inside the vacuum chamber is a tricky job. Condition of low pressure has to be maintained inside the chamber.
4. Special arrangement is needed for the collection of nanopowders.

5.4 Applications of gas phase condensation

The method of gas phase condensation used for the synthesis of nanomaterials has several applications in nanotechnology. These are listed below:

1. This process is highly suitable for the preparation of magnetic nanoparticles of cobalt.
2. This process is widely used in the production of ultra-fine powders for use in catalysis and optical devices.
3. This method is used for the synthesis of nanoparticles for gas sensing applications.

6 Vacuum deposition

Vacuum deposition also known as vacuum evaporation is a generic term of a typical surface treatment technology. The technology is used to deposit thin layers of materials onto a substrate. As the term suggests, vacuum deposition technologies must include processes that put source materials into a vapor state via condensation, chemical reaction, or conversion inside a vacuum environment.

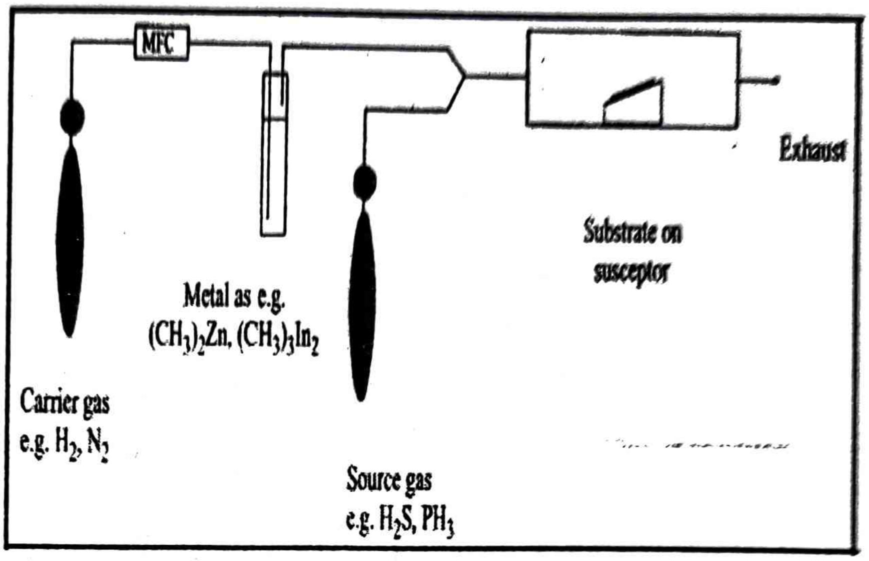

Figure 11: Schematic representation of a simple MOCVD apparatus. The reactor may be hot or cold walled.

When the vapor phase is produced by condensation from a liquid or solid source, the process is called physical vapor deposition (PVD) and when produced from a chemical reaction, the process is known as chemical vapor deposition (CVD). Schematic diagrams of MOCVD and vacuum deposition techniques are shown in Figures 11 and 12 respectively.

Principle of operation: After vaporization, atoms or molecules from the source reach the target surface known as the substrate in a vacuum environment without colliding with residual gas molecules between the source and the substrate in the deposition chamber. In order to avoid collisions, the mean free path of the molecules aiming the substrate should be very large which requires a vacuum better that 10 Torr inside the deposition chamber. At this pressure, there is still a large amount of concurrent impingement on the substrate by potentially undesirable residual gases that can contaminate the film deposited on the substrate. In such cases, a high (10 Torr) or ultrahigh (less than 10 Torr) vacuum environment is normally used to produce a film with the desired purity, depending on the deposition rate, reactivities of the residual gases and depositing species, and the tolerable impurity level in the deposit.

For the requirement of better vacuum, vacuum deposition technique had to wait until the discovery of Springer mercury-column vacuum pumps. Although sputtering and sputter deposition were reported in the mid-1800s using oil-sealed piston pumps,it took almost 70-80 years to achieve high or ultrahigh vacuum. In 1879, Edison used Springer mercury-column vacuum pumps to evacuate the first carbon-filament incandescent lamps and in 1887, Nahrwold performed the first vacuum evaporation. However, Vacuum deposition of metallic thin films was not common until the 1920s. Nowadays different types of vacuum deposition techniques are frequently used for the synthesis of thin films.

6.1 Advantage of vacuum deposition

Vacuum deposition method has several advantages for the synthesis of nanomaterials. These are listed below:

1. The particle density is reduced so that the mean free path for collision becomes longer.
2. The particle density of undesirable atoms and molecules (contaminants) is reduced.
3. It provides a low pressure plasma environment.
4. It provides a means for controlling gas and vapor composition.
5. It provides a means for mass flow control within the processing chamber.

Any Vapor deposition technique either PVD or CVD deposits a thin layer of source material onto the surface only keeping the bulk of the source relatively cool and unchanged. As a result, surface properties are modified typically without significant changes to the underlying microstructure of the substrate.

Vacuum deposition methods may be broadly classified into two categories: (i) **physical vapor deposition (PVD)** and (ii) **chemical vapor deposition (CVD)**. These two vacuum deposition techniques are discussed in detail in the following sections.

7 Physical vapor deposition (PVD)

Physical vapor deposition is a very popular vacuum deposition technique where a thin film of a source material is deposited over the entire substrate rather than in certain areas. The thickness of the deposited film can range from angstroms to millimeters. This particular technology is very versatile in nature and it can develop nearly homogeneous thin film of almost every type of inorganic materials such as metal, alloys, compounds and organic materials as well. Over the past few years the application of PVD technologies has been increased tremendously in different important sectors of science and technology namely engineering, chemical, nuclear, microelectronics and related industries. Since modern technologies demand multiple and conflicting set of properties materials which a single material can not fulfill. So, the only solution is therefore a composite material i.e a core material along with a coating each having requisite properties to fulfill the requirements.

The primary objective of this type of deposition process is to transfer atoms from a source material to the substrate in a controllable manner. In this process, whatever be the source material inorganic or organic, it must remain in solid or liquid state such that it can vaporize from a condensed phase and then back to a thin film condensed phase. Several methods are used to evaporate atoms from the source material and depending on that PVD variants differ from each other. For example, in thermal evaporation vaporization of source material is done through resistive heating, whereas in sputtering the same is done via bombarding the source material with a plasma (accelerated gaseous ions), or in electron beam evaporation the bombardment is done by electrons, in pulsed laser deposition (PLD) method a high intensity laser ablates material from the source into a vapor state.

The main categories of PVD processes are thermal evaporation, e beam evaporation, pulsed laser deposition, arc vapor deposition, ion plating etc. Some of these procedures are discussed in detail.

7.1 Thermal evaporation

Thermal evaporation is the simplest and first practical PVD technique for the synthesis of nanomaterials. It is normally used for the synthesis of a variety of oxide and non oxide thin films. The solid source material is evaporated through resistance heating and then thin layer of atoms are deposited on a substrate via condensation. Selection of a suitable source for resistance e vaporization is a critical issue, generally sources are made of refractory metals (Mo, Ta, W).

Principle of operation: The substrate on which the thin film is to be deposited is positioned facing the source. The pressure inside the vacuum chamber should be such that the mean free path of the evaporated atoms have the mean free path larger than the distance between the source and the substrate. A crystal monitor placed near the substrate records the quantity and rate of deposition. Normally the deposition rate in his particular PVD variant is few $\mathring{A}$ per seconds. Though this process is applicable for thin film preparation in photovoltaics, anti reflection coating in silicon based solar cells but requirement of high temperature (1000 to 1200^0C) and ultra high vacuum (10^{-6} Torr) are the prime limitations of this process.

7.1.1 Advantage of thermal evaporation

There are certain advantages of thermal evaporation. These advantages are listed below:

1. Simplest and economical among all PVD variants.

2. Solid material of any shape can be used as source material.

3. Rate of deposition is quite high and chances of damage of the substrate during deposition.

7.2 Electron beam evaporation

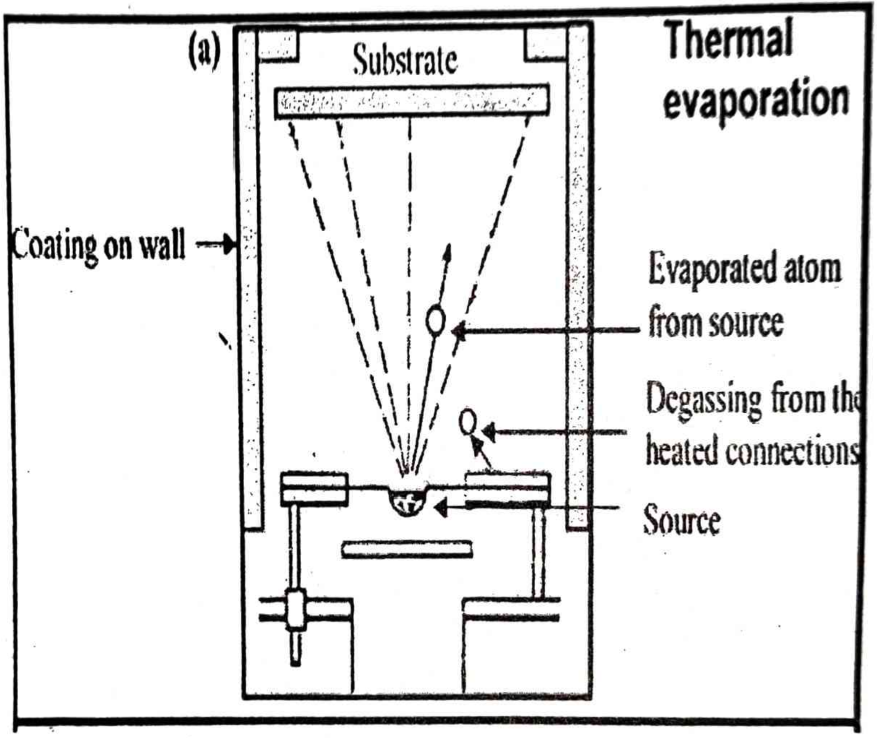
(a)
Substrate
Thermal evaporation
Coating on wall
Evaporated atom from source
Degassing from the heated connections
Source

Figure 12: Schematic diagram of Vacuum deposition.

Electron beam (E-beam) evaporation is a form of physical vapor deposition technique. In this technique, the target material to be used as a coating is bombarded with an electron beam from a charged tungsten filament to evaporate and convert it to a gaseous state for deposition on the material to be coated. The whole process takes place in a high vacuum chamber inside which atoms or molecules are in a vapor phase. Then these atoms or molecules precipitate and form a thin film coating on the substrate. Together with sputtering, E-Beam evaporation is the most common types of physical vapor deposition (PVD). Of these two processes, the E-Beam deposition technique has several clear advantages for many types of applications.

7.2.1 Instrumentation of Electron Beam Evaporation

The following entities are the key components of an electron beam evaporation technique: electron gun, magnetic focusing of the electron beam, target material in a water cooled crucible, focusing of the vapor atoms or molecules ejected from the target materials and finally deposition of these atoms or molecules on the substrate producing thin film of desired thickness of the yield significantly higher deposition rates - (from 0.1 nm per minute to 100 nm per minute) which results higher density film coatings.

E beam evaporation and sputtering are the two most common types of PVD processes. However, compared to the later one E beam evaporation has may advantages.

Compared to other PVD processes, E-Beam evaporation also has very high material utilization efficiency. in this process only the target source material is heated not the the entire crucible, resulting in a lower degree of contamination from the crucible. in such a way it helps to reduce the possibility of heat damage to the substrate.

Principle of operation: This is a widely used form of physical vapor deposition. In basic difference between thermal evaporation and E beam evaporation is that here the evaporation of the target material is done through a high energy electron beam instead of resistive heating.

7.2.2 Characteristics of the electron beam evaporation method

Characteristics of the electron beam evaporation are listed below:

1. As the heat source is the kinetic energy of the electrons, the target material is heated directly. This process is very efficient.
2. The electricity density of the electron beam is large, and evaporation of various materials is possible, including high melting point metals, as well as oxides compounds, and substances that sublimate.
3. The electron beam used in this process can be precisely controlled using electric and magnetic fields. The electron beam can be scanned at high speed within a specified area, and the beam can be irradiated with the optimal electric density for the target material.
4. Electron beams are deflected by 270^o or 180^o degrees and irradiated onto the evaporation material.
5. It is used in a high vacuum ($10^{-2} Pa \ to \ 10^{-5} Pa \ or \ so$). An ultra-high vacuum type is also available.
6. By using several crucibles and evaporation sources, it is possible to make a multi-layer film during a single processing sequence.

7.2.3 Application of Electron Beam Evaporation Technique

E-beam evaporation is available on a variety of PVD platforms and for many applications, including metalization, dielectric coating, optical coatings, and Josephson junctions. The electron beam evaporation process has a very high deposition rate and high efficiency of material utilization. As a result, this process is used in a wide variety of applications ranging from high performance aerospace and automotive industries to durable hard coatings for cutting tools. This technique also finds applications in chemical barriers and coatings that protect surfaces in corrosive environments like marine fittings and in optical thin films ranging from solar panels, eye glasses and architectural glass to give them the desired conductive, reflective and transmissive qualities.

Electron beam evaporation is used for optical thin films ranging from laser optics, solar panels, eye glasses and architectural glass to give them the desired conductive, reflective and transmissive qualities.

7.2.4 Advantage of electron beam evaporation technique

Electron beam evaporation has many advantages over resistive thermal evaporation. These advantages are briefly described below:

1. Firstly the e-beam source is capable of heating materials to much higher temperatures than is possible using a resistive boat or crucible heater. This allows for very high deposition rates and evaporation of high temperature materials and refractory metals such as tungsten, tantalum, or graphite.

2. Secondly, films deposited by electron beam evaporation can better maintain the purity of the source material; water cooling of the crucible tightly confines the electron beam heating to only the area occupied by the source material, eliminating any unwanted contamination from neighboring components.

3. Finally, electron beam evaporation sources are available in a variety of sizes and configurations including single or multiple pockets. Pocket indexing using a motorized carousel allows one source to deposit many materials from a single source location.

7.3 Pulsed laser deposition

Pulsed laser deposition (PLD) is a physical vapor deposition technique where a high power pulsed laser beam is focused to strike a target of the desired composition. Material is then vaporized and deposited as a thin film on a substrate facing the target. This process can occur in ultra high vacuum or in the presence of a background gas, such as oxygen when depositing films of oxides.

Pulsed laser deposition (PLD) is a physical vapor deposition process that has been used for producing high quality films of material over the past few decades. It is a prime method for producing metal oxide based (MOX) gas sensing layers.The technique attracts scientific

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2. **Ionization density of the ablated material**
3. **temperature of the surface of the substrate**
4. **Pressure of the background gas**
5. **Nature such as roughness of the surface of the substrate**

7.3.1 Some comments about laser used in pulsed laser deposition technique

Generally there are two approaches to pulsed laser deposition technique: conventional PLD and ultrafast PLD. These techniques make use of different pulsed-laser sources, resulting in different predominant ablation mechanisms. In conventional PLD, ultraviolet excimer gas lasers (F_2^* operating at 157 nm, ArF^* 193 nm, KrF^* 248 nm, $XeCl^*$ 308 nm, XeF^* 351 nm) provide nanosecond laser pulses of average energy ~ 0.0110 J, intensity ~ $10^8 10^9$ W/cm^2 and repetition rates ~ 150 Hz. The laser spot area on the target is typically 0.55 mm^2 but can be larger and non-circular in shape. Penetration depths are up to several micrometers, and depend strongly on laser power density and material absorption coefficient. Similarly, deposition rates can reach up to tens of nm per pulse (1024 nm per pulse or even more), and are likely difficult to control.

These conditions are associated with the thermal ablation mechanism, in which species are ejected from the target mostly by local thermal overheating, i.e. melting and vaporization. In contrast, electrostatic ablation dominates in ultrafast PLD. In this method, species (ions) are ejected from the target due to the strong electric fields. These fields are formed through charge separation by ionization, associated with electrons being emitted from the target. Ultrafast PLD uses pico-second or femtosecond pulsed lasers, e.g. higher harmonic generation in Nd:YAG laser (natural frequency at $\lambda = 1064.1$ nm) at 532, 355, 266 nm. The repetition rates reach ~ 50100 MHz, the intensities above ~ 10^{13} W/cm^2 and the average energy is in the μJ range. The penetration depths in the target, up to 12μm, are typically smaller than in conventional PLD. Deposition rates can be controlled easily and are 115 nm per pulse. Ultrafast PLD has the advantages of: (1) forming of a continuous flow of ablated species, (2) changing the ablation mechanism from thermal to electrostatic, and (3) smoothing the effective intensity distribution, allowing the creation of a single homogeneous phase in the ablated plume.

7.3.2 Advantages of Pulsed Laser Deposition Technique

There are some advantages of the pulsed laser deposition process for the fabrication of thin films of nanometer thickness. These advantages are listed below:

1. Thickness of the deposited film and its structure can be controlled by varying deposition parameters such as laser fluence, background gas pressure substrate temperature, roughness of the substrate surface etc.

2. The flexibility in wavelength and power density allows the process to ablate many material or materials combination by selecting the appropriate laser wavelength in order to match the absorption properties of materials.

3. Large pressure range to deposit target materials on the substrate: from $< 10^{-7}$ mbar (vacuum without additional background gas) up to 1 mbar.

4. The laser is not part of the vacuum system. Therefore, a considerable degree of freedom in the ablation geometry is possible.

5. The use of a pulsed laser beam enables precise control over the growth rate (sub-monolayer per pulse).

6. The congruent transfer of the composition can be achieved for many ablated material or materials combinations.

   Moderation of the kinetic energy of evaporated species to control the growth properties and growth modes of a film. In addition, a background gas can provide an appropriate reactive atmosphere using e.g. oxygen to create oxide species in the plasma, when growing oxide films.

7. Controlled preparation of nanoparticles by femtosecond-PLD.

8. The deposition rates are relatively high typically ~ 100 $\AA$/min and can be achieved at moderate laser fluences.

9. Since a laser is used as an external energy source, it results an extremely clean process without filaments. Thus deposition can occur in both inert and reactive background gases.

10. The ablation geometry can be changed with considerable degree of freedom.

11. The kinetic energy of the evaporated species can be controlled to have known properties and growth modes of the film.

7.3.3 Disadvantages of pulsed laser deposition (PLD) technique

There are also disadvantages associated with the PLD process. Some of them are of a technical nature; some are intrinsic to the ablation process and the electromagnetic interaction between photons and matter. These disadvantages are listed below:

1. The plasma plume created during the laser ablation process is highly forward directed, therefore the thickness of the material deposited on a substrate is highly non-uniform and the composition can vary across the film. The area of deposited material is also quite small, typically ~ 1 cm^2, in comparison to that required for many industrial applications which require area coverage of ~ (7.5 × 7.5) cm^2.

2. The ablated material also contains macroscopic globules of molten material, up to ~ 10 μm diameter. The arrival of these particulates at the substrate is obviously detrimental to the properties of the film being deposited.

3. The large kinetic energy of some plume species causes re-sputtering and likewise defects in the substrate surface and growing film.

4. An inhomogeneous energy distribution in the laser beam profile gives rise to an inhomogeneous energy profile and angular energy distribution in the laser plume.

5. Light elements like oxygen or lithium have different expansion velocities and angular distributions in a plume as compared to heavier elements. To obtain the desired film composition, e.g. an adapted target composition or a background gas is required.

6. Due to the high laser energies involved, macroscopic and microscopic particles from the target can be ejected which can be detrimental to the desired properties of films and multilayers.

7. The fundamental processes, occurring within the laser-produced plasmas, are not fully understood still today; thus deposition of novel materials usually involves a period of empirical optimization of deposition parameters.

In spite of all these advantages and disadvantages, PLD techniques are widely used for fabricating super quality crystalline films, for deposition of ceramic oxide, nitride films metallic multi layers. Another very important use of this PVD technique is that it is used for the production of superconducting and insulating circuit components.

8 Chemical vapor deposition (CVD)

Chemical vapor deposition is generally a bottom up approach, used to deposit a thin film of a solid target material from its vapor phase.This process is extremely popular for producing thin films of semiconductors, composites, Nanomachines, optical fibres, catalyst, etc. Micro fabrication process generally use CVD to deposit thin films of various types of materials such as compounds of silicon (oxide, carbide, nitride etc), different forms of carbon (fibre, nanofibre, nanotubes, diamond, graphene etc), tungsten, etc.

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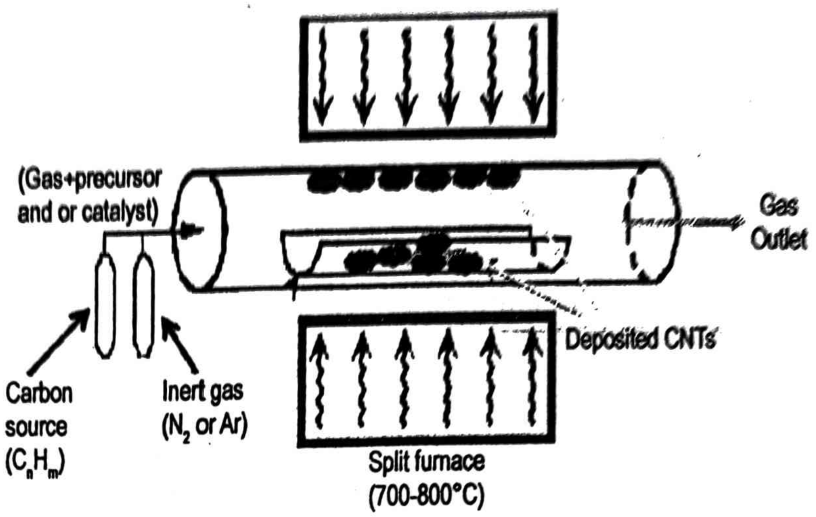

Figure 15: Schematic diagram of a CVD apparatus.

Chemical vapor deposition is a hybrid method using chemicals in vapor phase. This method is conventionally used to obtain coatings of a variety of materials from inorganic to organic. This method is widely used in industry because of its relatively simple instrumentation, ease of processing, possibility of depositing different types of materials and economical viability. Under certain deposition conditions, It is also possible to prepare nanocrystalline or single crystalline films in this method. There are many variants of CVD processes like metallo organic CVD (MOCVD), atomic layer epitaxy (ALE), vapor phase epitaxy (VPE), plasma enhanced CVD (PECVD) etc. These processes differ in source gas pressure, geometrical layout, temperature etc. Basic CVD process, however, can be considered as a transport of reactant vapor or reactant gas towards the substrate kept at some high temperature where the reactant cracks into different products and diffuse on the surface. These diffused reactant gases undergo some chemical reaction at appropriate site, nucleate and grow to form the desired material film. The by-products created on the substrate are transported back to the gaseous phase removing them from the substrate.

Principle of operation: A schematic diagram of CVD is shown in Figure 15. A typical CVD apparatus consists of a gas supply system, reactor chamber, substrate loading mechanism, energy source, vacuum system, exhaust system and process control equipment. Each and every component has its own utility. A schematic diagram of a CVD apparatus is shown below. Basic principle of CVD is somewhat similar to PVD. In CVD the material is coated on a substrate material. It is basically a process of diffusive convective transport. The target material is sent to a reaction chamber in the form of vapor at a certain temperature. Normally CVD processing temperatures are quite hig, it typically lies in the range of 850 to 1100^0C. Inside the reaction chamber, the gaseous target material is transported to the substrate and the gas reacts with the substrate and gets deposited on to it. The temperature of the substrate is crucial for determining the deposition so the temperature and pressure inside the apparatus should be controlled significantly and pretreatment of the substrate is also required. Finally, the apparatus should have a way to remove the excess gaseous waste out. The coating material (sometimes termed as precursor) should be volatile as well as stable in order to be converted

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to the gaseous phase and then coat onto the substrate. Generally precursors compounds will provide a single element to the deposited material, with others being volatilized during the CVD process. In some cases, precursors may provide more than one element. Such materials actually simplify the delivery system as they reduce the number of reactants to produce a given compound. CVD precursors can be grouped into a number of catergories such as hybrides, halides, metal carbonyls, metal alkyls, and metal alkoxides etc.

8.1 Characteristics of CVD coatings

These are the characteristics of coatings formed in chemical vapor deposition technique:

1. The coatings are fine grained.
2. The coatings are impervious i,e do not allow fluid to pass through it.
3. The purity of the coatings are very high.
4. The coatings are harder than similar materials produced using conventional ceramic fabrication processes.
5. The thickness of CVD coatings are usually of the order of a few micron and are generally deposited at fairly slow rates.

8.2 Advantages of chemical vapor deposition technique

These are the advantages of chemical vapor deposition (CVD) technique.

1. CVD is suitable for large area thin film deposition.
2. It is used to deposit super quality films and augment the substrate surface in such a way that can't be done via traditional surface treatment technologies. It is extremely useful in atomic layer deposition (ALD) process.
3. CVD is widely used in semiconductor industry. $GaAs$ thin films deposited by this technique are used in integrated circuits and photovoltaic cells.Polymerization by CVD allows super thin film deposition having some desirable quality such as lubricity, hydrophobicity, weather resistance etc.

8.3 Comparison between PVD and CVD

PVD and CVD are coating techniques. PVD stands for physical vapor deposition while CVD stands for chemical vapor deposition. The key difference between PVD and CVD is that the coating material in PVD is in solid form whereas in CVD it is in gaseous form. As another important difference between PVD and CVD, we can say that in PVD technique atoms are moving and depositing on the substrate while in CVD technique the gaseous molecules will react with the substrate.

Moreover, there is a difference between PVD and CVD in the deposition temperatures as well. That is; for PVD, it deposits at a relatively low temperature (around $250^oC \sim 450^oC$) whereas, for CVD, it deposits at relatively high temperatures in the range of 450^oC to 1050^oC.

8.4 Difference between physical vapor deposition technique and chemical vapor deposition techniques

TABLE I

No. of observations	PVD	CVD
1	PVD is a physical vapor deposition.	CVD is a chemical vapor deposition.
2	PVD is performed in a solid form.	CVD is performed in a gaseous form.
3	Atoms are in a moving state and are deposited on the substrate.	The gaseous molecules react with the substrate.
4	Atoms or molecules are deposited at relatively low temperature (around $250^oC \sim 450^oC$).	Gaseous molecules are deposited at relatively high temperatures in the range of 450^oC to 1050^oC.
5	This method is suitable for coating tools that are used in tough cutting edge applications.	This method is mainly used for depositing compound protective coatings.

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8.5 Sol-gel process

Chemical methods are used frequently to synthesize nanomaterials. Chemical methods include sol-gel process, colloidal, electro-deposition, Langmuir - Blodgett (LB) films, inverse micelles etc. In some chemical processes, nanomaterials are obtained as colloidal particles in solutions. These solutions are filtered and dried to obtain powder of the nanoparticles. In some chemical methods, thin films or nonporous materials are obtained by electro-deposition, etching etc. The chemical method of synthesis has several advantages which are listed below:

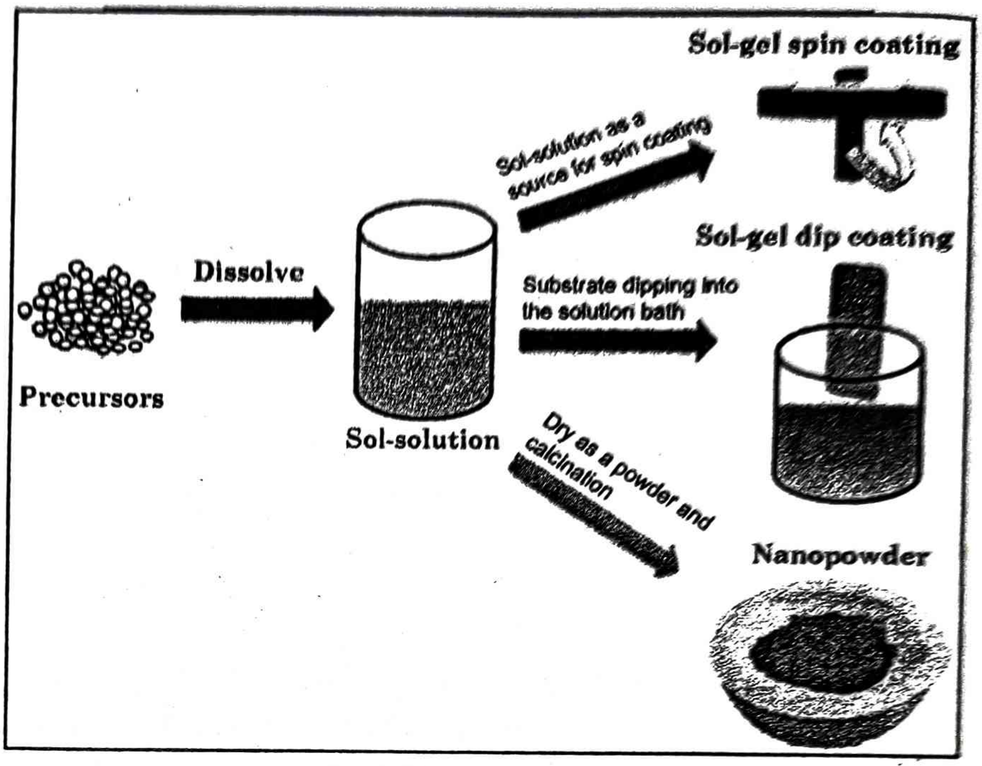
Sol-gel spin coating
Sol-solution as a source for spin coating
Sol-gel dip coating
Dissolve
Substrate dipping into the solution bath
Precursors
Sol-solution
Dry as a powder and calcination
Nanopowder

Figure 16: Schematic diagram of steps involved in sol gel process.

1. The techniques used in this method are simple.
2. The method is inexpensive and less instrumentation is required compared to other physical methods.
3. In this this method, temperature ($< 350^oC$) for synthesis is low.
4. During synthesis, doping of foreign atoms (ions) is possible in this method.
5. Large amounts of the substances can be received.
6. Products are available in various kinds of shapes and sizes.
7. Initially substances are received in the form of liquid but then be converted into dry powder or thin films quite easily.
8. Self assembly or painting is possible in this method.

Generally the nanoparticles synthesized by chemical method are obtained in 'colloids' forms. The processes like sol-gel and colloidal will be discussed in detail to obtain nanoparticles via chemical routes.

Chemical route is one of the best synthesis methods for preparing good quality and homogeneous nanomaterials. Among various chemical methods, sol-gel is one of the processes. It is a low temperature, highly controllable and cost effective method for the production of nearly homogeneous, highly stoichiometric and high quality ultrafine nanostructures. This route is the most acceptable one to produce desired shape of the metal oxide nanostructures such as nanospheres, nanorods, nanoflakes, nanotubes, nanoribbons, nanospheres and nanofibers etc. Ebelman developed silica gel by this technique in 1846 and since then this method has been developed progressively and nanomaterials are being synthesized routinely via this process. These nanomaterials are being implemented in several scientific and technological applications with excellent optical, magnetic, electrical, thermal and mechanical properties.

Principle of operation of sol-gel process:

The schematic diagram of sol-gel method is presented in Figure 16. The experimental set up is very simple. Two things are initially required for this process. One is the solvent and the other is the solute. The process involves conversion of monomers into a colloidal solution known as the 'sol'. The sol can also be deposited onto a preferred substrates as thin films using two techniques: (1) spin coating and (2) dip coating.

The 'sol' gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. This gel is used to form materials of different types such as nanoparticles, xerogel, glass or ceramics etc. depending upon the further processing steps involved. Nanoparticles and xerogels are then obtained by simple evaporation of solvent. The xerogel can also be formed as ceramics by heat treatment and glassy nature of the ceramics can be induced by melting techniques.

Normally, for production of the nanoparticles, after the formation of gel, it must be heated up to the stage where all the sample gel is burned. Generally then a black floppy and dried mass is formed. This dried mass is then grinded and pelletized and finally sintered at the required temperature to obtain the desired compound.

8.5.1 An example of sol-gel method: preparation of La_2NiMnO_6 nanoparticles

As a typical example of sol-gel process, preparation of a double perovskite compound is discussed below.

A series of La_2NiMnO_6 ($LNMO$) nano sample can be synthesized via sol·gel process. Stoichiometric amounts of high purity (99 : 999%) lanthanum oxide (La_2O_3) and nickel powder are mixed with nitric acid to form lanthanum nitrate ($La(NO_3)_3; 6H_2O$) and nickel nitrate ($Ni(NO_3)_2; 6H_2O$). These nitrate solutions and manganese acetate ($Mn(CH_3COO)_2; 4H_2O$)

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are then mixed with citric acid to form the gel. Then the formed gel is dried up and made in powder form. Finally the dried gel (in powder form) is annealed in air for 12 hours at a particular temperature. This temperature is called the anealing temperature which affects the grain size of the final product. For example, in this double perovskite compound La_2NiMnO_6, grain sizes are $\sim 43 \pm 5.05\ nm$, $\sim 54 \pm 4.32\ nm$ and $\sim 71 \pm 4.98\ nm$ when the sample is annealed respectively at $700^o\ C$, $800^o\ C$ and 900^oC. This indicates that with annealing temperature, grain size increases.

8.5.2 Advantage of sol-gel method

Sol-gel method has several advantages for the synthesis of nanoparticles. Some of the advantages are listed below:

1. In sol-gel method, several forms of materials such as thin films, nanoparticles, glass and ceramics can be achieved in a cost effective way.
2. It requires low temperature chemistry and the final products are easily reproducible in this process.
3. High surface to volume ratio of the final products is the most significant feature which adds merit to this synthesis process.
4. This synthesis process provides smaller particle size and control over the morphological aspect of the sample.
5. For thin film deposition, sol-gel is the cheapest having fine control on the chemical composition of the products.

8.5.3 Disadvantage of sol-gel method

Apart from the above mentioned advantages, there are some disadvantages of this synthesis method. These disadvantages are described below:

1. It uses high purity raw materials which are not cost effective as compared to mineral based metal ion sources.
2. Since it is a multi step process, it requires regular monitoring.
3. It is difficult to avoid OH-groups and residual porosity.
4. The process is not very clean. It contains undesired atoms, molecules, ions etc. As a result, electrical and optical properties of deposited material deteriorate.

5. There is often a large volume shrinkage and cracking during drying the gel.

Sol-gel process has been extensively explored for production of the metal oxide nanostructures in the field of engineering and technological applications. This is due to the controlled shape and size exhibited by the final products available in this process. This route is preferred for synthesis of metal oxide-based nanostructures with several ranges of applications such as magnetic, energy generation, conversion and storage devices, electronic device applications and sensors and actuators materials. Moreover, biomedical applications involving drug deliveries, mimicking of natural bone and teeth, anti-microbial activities and pharmaceuticals employ sol-gel prepared metal-oxide nanostructures because of their low temperature synthesis, homogeneity and purity.

8.6 Electrodeposition

Electrodeposition, also known as electroplating, is an electrochemical process that allows the preparation of solid deposits on the surface of conductive materials. It belongs to the category of bottom up approach of synthesizing nanomaterials. Since thin films are being extensively used in microelectronics, this fabrication technique is receiving greater attention to produce thin films of some material to the surface of another material to change its external properties such as to increase corrosion protection, increase abrasion resistance, improve decorative quality, or simply to deposit a layer which is part of a more complicated device. This method is a commercially highly relevant process, providing the basis for many industrial applications such as electro-winning, refining, and metal plating. For example, nickel metal is electroplated on automotive products so as to inhibit against corrosion, and copper metal is electro-deposited on to circuit boards to provide low resistance pathways between electronic components.

Principle of operation: Electrodeposits are formed by the action of an electric current passing in an electrochemical cell. We know that an electrochemical cell is a device that consists of two conductive or semi-conducting electrodes immersed in an electrolyte. The electrodes used in electrodeposition are called the working electrode (cathode) that consists of the object where electrodeposition is planned, and the counter-electrode (anode) necessary to complete the electrical circuit. Electrolytes for electrodeposition are usually aqueous solutions containing positive and negative ions, prepared by dissolving metal salts. The electric current that flows between the two conductive electrodes, in presence of an external voltage, is because of the motion of charged species via migration and diffusion, towards the surfaces of the polarized electrodes. At the surface of the electrodes, the conduction mechanism changes from ionic to electronic and this is an intermediate process mediated by the occurrence of electrochemical reactions that promote the reduction or the oxidation of the ionic species.

Electrodeposition on the industrial scale requires an electrochemical cell and a DC current power supply. This approach is relatively simple and inexpensive, and is known as galvanostatic

3Y

plating system, because the current between the electrodes is controlled (maintained constant). Another important deposition mode is the pontentiostatic one as shown schematically in Figure 17. It consists of three electrodes, namely working, reference, and counter (sometimes secondary) electrodes, respectively. This mode is a consequence of the development of electrochemical science, where electrochemical reactions at the surfaces of electrodes are carefully investigated. The electrodes are kept within a vessel containing a liquid which has ionic species dissolved within it, such as copper ions dissolved in water. The working electrode is the object that is to be plated, the counter electrode is used to complete the electronic circuit, and the reference electrode is used as a fixed reference point for the potentiostat. The electrochemist developed reference electrodes, in order to measure the potential drop near the surface of electrodes. A simple metal foil could be used as a reference electrode. However, because of the need to have a standard electrode to measure potential drops at the surface of different types of working electrodes in contact with different electrolytes, a hydrogen electrode is elected. At present, all electrode potentials are quoted relative to this arbitrarily chosen reference electrode. Some other reference electrodes are also frequently used in the laboratory which are robust, stable, and easily constructed than the standard hydrogen electrode (SHE). These reference electrodes provide potential measurements that can be converted to standard potentials by adding or subtracting a constant value. The most common of such reference electrodes are the calomel electrode (Hg/Hg_2Cl_2) and silver/silver chloride electrode ($Ag/AgCl$).

The electrodes are connected to a potentiostat, an instrument which controls the deposition process. An electric field is then applied across the working electrode in such a way as to give electrons to the ions in solution so that they form uncharged elements or compounds which prefer to adhere to the surface of the working electrode rather than remain dissolved in solution. The strength of the electric field or the potential is measured with the reference electrode (and calibrated), but the actual current flows between the working and counter electrodes.

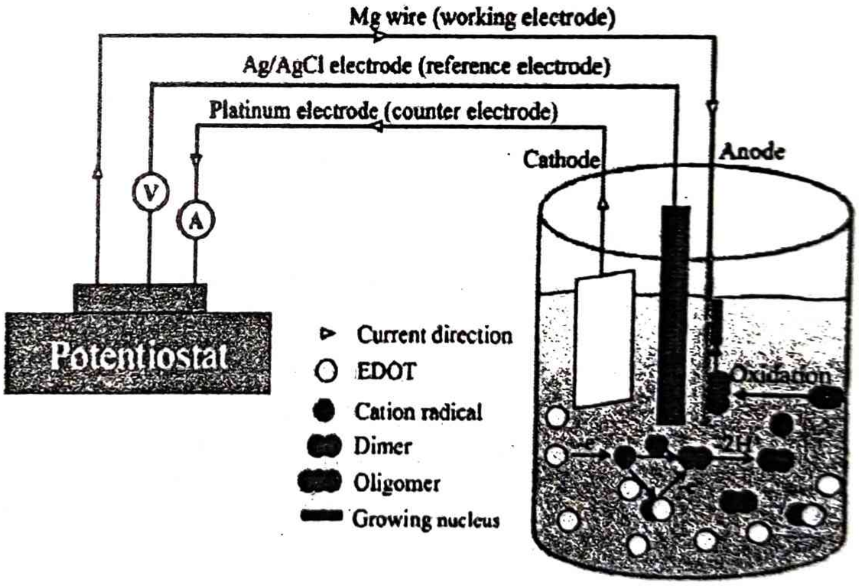

Figure 17: Schematic diagram of electrodeposition process using a potentiostat.

Thin films deposited via electrodeposition are mechanically strong and uniform. It has been observed that certain properties of the nanostructured deposits such as hardness, wear resistance and electrical resistivity are strongly affected by the grain size. Superior coating performance is realized as a combination of increased hardness and wear resistance. Nanowires consisting of alternating magnetic and non-magnetic layers and single electron transistors using niobium are fabricated using this method of electrodeposition.

8.6.1 Advantages of electrodeposition

The following features provide the advantages of electrodeposition:

1. It is relatively cheap and fast process.
2. It has high utilization rate of raw materials and it is a low energy consumption process.
3. The most important thing is that this process can be performed at room temperature.
4. The material waste in this process is very low.
5. It is an exceptionally versatile process.
6. This technique provides precise control of film thickness, morphology, stoichiometry, and doping.
7. Thin films fabricated by electro-deposited are mechanically strong and nearly uniform in thickness.

8.6.2 Applications of electrodeposition

These are several applications of electrodeposition. These are listed below:

1. This process can be used to grow functional materials through complex 3D masks.
2. Since it is performed near room temperature, it is economically viable to produce low cost materials which find applications in daily life.
3. The process can be scaled down to the deposition of a few atoms. So it finds wide applications in nanotechnology.
4. Polymers and biomaterials are electrodeposited for biomedical applications.
5. Metal oxides and compound semiconductors are grown via this method for electronic and optoelectronic applications.

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8.7 Spray Pyrolysis

The spray pyrolysis technique is a low-cost, non-vacuum way to synthesize nanomaterials in the form of powders and films. It also belongs to the category of BOTTOM UP APPROACH of synthesizing nanomaterials. Very often, for investigation of physical properties, it is required to deposit films over a wide variety of substrates. This can be easily adapted via this process of spray pyrolysis for large area deposition and industrial production. This technique has been extensively used to synthesize materials for a wide variety of applications such as micro and sub-micrometer dimension MOSFETs for integrated circuits technology, light emitting devices for displays and solid-state lighting, planar waveguides and other multilayer structures for photonic devices.

Principle of operation: Spray pyrolysis is a process in which a thin film is deposited by spraying a solution (by forcing it through a hole or nozzle at high pressure) on a heated surface, where the constituents react to form a chemical compound. This technique involves three major process stages: precursor solution composition, aerosol generation and transport, and synthesis. Each one of these stages is tuned according to the final chemical and physical characteristics of the material targeted. The choice of materials/processes at each stage and the corresponding adjustments affect the rest of the stages to some extent. At the first stage, the chemical composition of the precursor solution involves a compound(s) that will render after the pyrolysis stage the chemical composition required. The selection of the solvent limits the maximum concentration of the precursor compound in the solution and determines the best choice for the aerosol generation/transport process and temperature and rate of synthesis. At the second stage, the proper range of synthesis temperatures is determined and the aerosol droplet size distribution, determined by the aerosol generation mechanism, sets the morphological characteristics of the final material produced. At the last stage, the final chemical reaction takes place on a gas phase or on a hot substrate determines whether the material synthesized is a powder or a film coating.

According to the types of reactions, the chemical spray deposition process are divided into three groups: In the first group, the droplets of the solution reside on the heated surface and the solvent evaporates. The components may further react in the dry state. The second group represents a process in which the solvent evaporates before the drops reach the heated surface and the dry solid impinges on the surface by decomposition. In the third group, there are processes where the solvent vaporizes as the droplets approach the substrate with the consequent heterogeneous reaction of the solution components. The most important parameters to be controlled in all of these processes are the substrate temperature, flow rate of the carrier gas, distance between the nozzle and the substrate, and the amount and concentration of the solution. Among these variables, the substrate temperature is considered to be the most important factor in producing thin film from spray pyrolysis processing. This is because the droplets drying, decomposition, crystallization, and grain growth depend strongly on this parameter.

The main part of the apparatus used for the spray pyrolysis deposition is the atomizer for obtaining aerosol from the precursor solution.

The design of the equipment in spray pyrolysis can be variable from inexpensive cosmetics or perfume purpose atomizers, through a Pyrex glass or metallic individual or commercial design atomizers to much more complicated ultrasonic equipments. Despite the apparent simplicity of the spray pyrolysis technique, a tight correlation of the deposition parameters is required for a theoretical modeling of the deposition process using spray pyrolysis technique. Such modeling examines the changes produced in the films topography, where the droplets can be seen as a flux and not as individual drops, and when they evaporate near the surface prior to fully contacting the substrate in liquid form. A typical spray deposition system includes the spray atomizer containing the precursor solution, a heater for the substrate, pressurized air, liquid flow, and temperature controllers. All these components of spray pyrolysis techniques are shown schematically in Figure 18. It is to be mentioned here that the thickness of the film in this spray pyrolysis is inherently non-uniform. Hence a random motion of the spray nozzle or the substrate is useful for a uniform deposition.

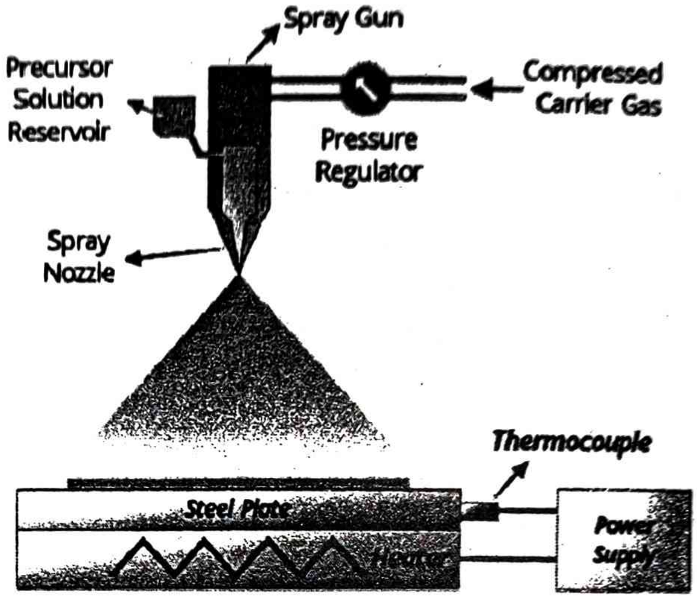

Figure 18: Schematic diagram of spray pyrolysis process.

"SPRAY PYROLYSIS IS THE AEROSOL PROCESS THAT ATOMIZES A SOLUTION AND HEATS THE DROPLETS TO PRODUCE SOLID PARTICLES". The Aerosol process is defined as the process in which a suspension of solid or liquid particles occurs in a gas. Droplets are produced through atomization and are dispersed into the gas. Spray pyrolysis takes place in the following steps:

1. Generation of aerosol and its transport.
2. Impact of droplet with consecutive spreading and
3. Decomposition of precursor.

8.7.1 Advantages of spray pyrolysis

These are several advantages of spray pyrolysis. These are listed below:

1. It is an extremely easy technique for preparing thin film of any composition.
2. This method is relatively cost effective.
3. It does not require high purity chemicals.
4. It can be performed in a space where vacuum is not necessary for area thin film deposition.

Apart from all these advantages, one major disadvantage of this process is that it often results in aggregates and agglomerates rather than singlet primary particles.

8.7.2 Applications of spray pyrolysis

These are several applications of spray pyrolysis. These are listed below:

1. This method is for deposition of dense films and porous films.
2. This method can also be used to deposit multilayer films.
3. It is used in glass industry and in the production of solar cell.

8.8 Hydrothermal synthesis

Hydrothermal synthesis is a solution reaction based approach. Schematic diagram using this process is shown in Figure 19. It is the technique of crystallizing substance from high temperature aqueous solutions at high vapor pressure. It is a bottom up approach for the synthesis of single crystal that depends on the solubility of minerals in hot water under high pressure. Water plays two important roles as transmitting pressure throughout the medium and solvent for the precursors. In order to control the morphology of the material to be prepared either low or high pressure conditions may be used depending on the vapor pressure of the main composition in the reaction.many types of nanomaterials may be synthesized using this technique. This is mainly used in the fabrication of synthetic quartz, gems and other single crystals having commercial value, and in the synthesis of metal and metal oxide nanoparticles.

Principle of operation:

Figure 19 shows schematically the procedures adopted in the hydrothermal synthesis technique. The setup includes a tubular reactor consisting of two parts, each approximately 3 m in length with inner diameter approximately 1.75 mm. There are also two piston pumps, syringe pump, back pressure valve, electric furnace with fluidized sand bed, cooler, flow mixer, manometers and pressure gauges. All syntheses of metal oxides are carried out virtually by the same procedure. The initial parent solution for synthesis is prepared by dissolution in water of equimolar or different molar amounts of nitrate, sulfate or acetate of the first metal, M_1, with other salt of the second metal, M_2. The parent solution is then introduced by a syringe pump into mixer 9 in a 1:10 ratio to supercritical water, which is introduced into the same mixer by a piston pump in a continuous mode. Transformations are performed at temperatures and pressures close to critical parameters of the mixture containing more than 95% percent of water, temperature above 371°C and pressure exceeding 230 atmosphere. These are the main parameters to be set for the synthesis for a typical nanoparticles using this method.

This process can be performed following any of the three methods: (i) temperature difference technique; (ii) temperature reduction technique and (iii) metastable phase technique. However, the method (i) is widely used and the super saturation in this method is achieved by reducing the temperature in the area of crystal growth. In method (ii), super saturation is achieved by a gradual reduction in temperature of the solution in the autoclave. The disadvantage of this method (ii) is the difficulty in controlling the growth process and introducing the seed crystal.

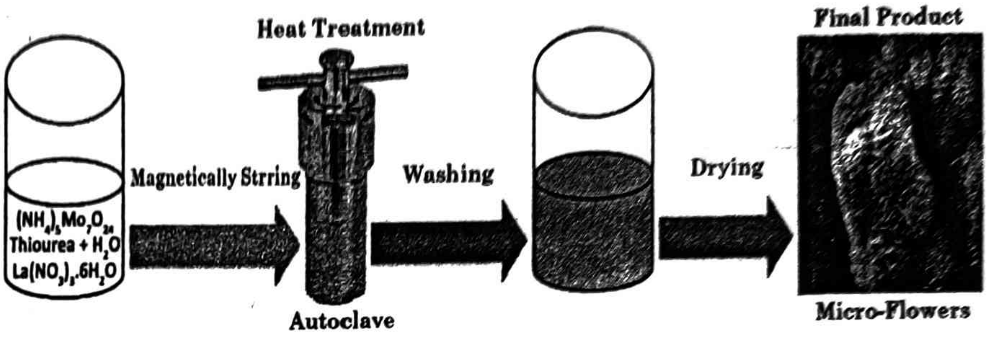

Figure 19: Schematic diagram of production of micro-flower using hydrothermal synthesis method.

8.8.1 Advantages of hydrothermal solution

This method has the following advantages for the synthesis of nanomaterials:

1. This method is suitable for the synthesis of nanomaterials which are not stable at the melting point.
2. Nanomaterials with high vapor pressure can be synthesized via this method with minimum loss of materials.
3. The composition of the nanomaterial to be produced can be well controlled in this method through liquid phase or multiphase chemical reaction.
4. This method is simple to implement and scale up.

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5. In this method, the particle size, morphology and physical properties of nanomaterials can be controlled by using different starting materials and changing one of the possible processing variables.
6. This synthesis method is a rapid technique that can produce high product yields.
7. This method allows control over particle size and their properties.
8. Powders can be formed directly from the solution.

8.8.2 Disadvantages of hydrothermal synthesis process

In spite of several advantages of this process, there are several disadvantages too. These are listed below:

1. Essential drawback of this synthesis procedure is its lesser control over the aggregation of nanoparticles. It is difficult to remove particles from solutions without agglomeration.
2. Another disadvantages are accidental explosion of the high pressure vessel and presence of corrosive slurries.
3. Costly autoclaves are required in this method.
4. The crystal cannot be observed during the process of its growth.
5. Prior knowledge on solubility of starting materials is required.

8.8.3 Applications of hydrothermal synthesis process

The following are the fields where hydrothermal synthesis process is applied:

1. This method is used to grow quartz and single crystals.
2. Metal and metal oxide nanoparticles are mainly synthesized in this method.

9 Colloidal methods

The colloidal method involves in formation of nanosized particles within a continuous fluid solvent matrix. Ultrafine particles (size ranging from 10^{-7} to 10^{-9} m) are suspended in the dispersing medium to form a colloidal solution. In this method, the monodispersed system is found to have high energy state, which is equivalent to the free energy required to fabricate the increased surface area. Due to the attractive inter-molecular forces (also known as van der Waals interaction), the colloidal suspension tends to aggregate and large particles are generated. In order to prevent particles from aggregation, the dispersing agents or surfactants are introduced to the colloidal systems. The energy barrier to agglomeration is highly dependent on the balance of attractive (van der Waals forces) and repulsive forces between the particles. The colloidal solution displays properties as a Brownian motion and it is the energy, which can be expressed as product of K_BT.

Table I. A summary of different types of colloids.

Serial No	Colloid Type	Dispersed Substance	Dispersing Medium	Example
1	Aerosol	Liquid	Gas	Fog
2	Aerosol	Solid	Gas	Smoke
3	Foam	Gas	Liquid	Whipped cream
4	Solid foam	Gas	Solid	Marshmallow
5	Emulsion	Liquid	Liquid	Milk
6	Solid emulsion	Liquid	Solid	Butter
7	Sol	Solid	Liquid	Paint; cell fluid
8	Solid sol	Solid	Solid	Opal

The particles with ultrafine sizes such as quantum dots are wisely used as semiconductors. This type of materials can be produced by impregnation suitable semiconductors into the glass matrix and followed by heat treatment. By this approach, the size of quantum dots can be controlled between 1 and about 40 nm, depending on the change of temperature and heating time. As a result, the electrical injection of carriers can be prevented due to the presence of insulating glass matrix. The injection of organometallic compounds allows for formation of $II-VI$ semiconductor quantum dots. The crystalline metal and metal oxide nanomaterials can be easily formed from an aqueous solution and the size can be tuned within 110 nm according to the addition of different dispersing agents, such as traditional Indian medicinal natural compounds. Due to the steric hindrance effects, the nanoparticles displayed high uniformity and tunable functionality. The polymeric grafting and functionalization of nanoscaled metal oxides change the band gap energy and magnetism. Accordingly the surface area, reactivity sites, and optical efficiency can be modified. Colloidal suspension of nanoscale noble metals and core-shelled alloys are found to exhibit excellent optical properties and long-term stability even in stand-alone formulations. These colloids can be incorporated into or deposited onto substances by spin casting or screening printing to form thin films with different thicknesses, which may allow for rapid ionic conductivity.

Recently a new method has been developed by researchers for the synthesis of highly dispersive inorganic nanoparticles with narrow size distribution. The limitations of earlier methods (e.g. bulky reaction under constant Argon flow with a heating mantle operating at 240°C) are overcome by a novel heating process that features a high ramping rate, producing high crystallinity of the nanoparticles. This novel method of synthesis is fit for safe, large-scale, reproducible, and energy efficient production of colloidal nanoparticles. In addition, this method allows for the mass production of colloidal nanoparticles that can enhance the sensitivity and specificity of biological sensors.

This method is generally applied to produce the following nanoparticles:

1. Biological sensing and tagging
2. Optoelectronic devices
3. Solid-state lighting
4. Solar cells

9.1 Advantage of preparation through colloidal methods

The advantages of this method for the synthesis of nanoparticles are the following:

1. Energy efficient
2. Reproducible for large-scale production
3. Cost-effective

9.2 What are quantum dots?

Quantum dots (QDs) are tiny semiconductor particles a few nanometers in size, having optical and electronic properties that differ from larger particles due to quantum mechanics. When the quantum dots are illuminated by UV light, an electron in the quantum dot can be excited to a state of higher energy. In the case of a semiconducting quantum dot, this process corresponds to the transition of an electron from the valence band to the conduction band. The excited electron can drop back into the valence band releasing its energy by the emission of light. This process of light emission is termed as the photoluminescence. The color of that light depends on the energy difference between the conduction band and the valence band.

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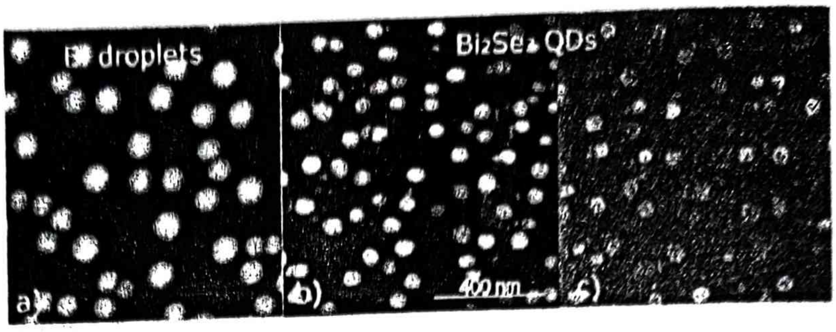

Figure 20: Atomic force microscopy images of (a) bismuth droplets and (b) Bi_2Se_3 quantum dots are shown in the figure. Scanning electron microscopy image of Bi_2Se_3 quantum dots is shown in (c). All pictures have the same scale.

Quantum dots have properties intermediate between bulk semiconductors and discrete atoms or molecules. Their optoelectronic properties change as a function of both size and shape. Larger quantum dots of 56 nm diameter emit light of longer wavelengths, with colors such as orange or red. Smaller quantum dots (23 nm) emit shorter wavelengths, yielding colors like blue and green. The specific colors, however, vary depending on the exact composition of the quantum dots.

In Figure 20, self-assembled Bi_2Se_3 quantum dots (QDs) on $GaAs$ substrates prepared by molecular beam epitaxy using droplet epitaxy technique is shown. Generally these QDs are characterized by atomic force microscopy and scanning electron microscopy and the quality of QDs are determined by Raman spectroscopy. These Bi_2Se_3 QDs are crystalline with hexagonal shape, and have average dimensions of 12 nm height (12 quintuple layers) and 46 nm width, and a density of 8.5×10^9 cm^{-2}. The size of such QDs can be varied in a controlled and reproducible manner by adjusting the growth parameters such as Bi deposition temperature and time.

10 Molecular Beam Epitaxy (MBE) Growth of Quantum Dots

Molecular Beam Epitaxy (MBE) is an advanced ultra-high-vacuum facility to make compound semiconductor materials with great precision and purity. These materials are layered one on top of the other to form semiconductor devices, such as transistors and lasers, and novel materials for research and development.

MBE is an epitaxy method for thin-film deposition of single crystals. This process was developed by J. R. Arthur and Alfred Y. Cho in the late 1970s at Bell Telephone Laboratories. It is widely used in the manufacture of semiconductor devices, including transistors, and it is considered one of the fundamental tools for the development of nanotechnologies. MBE is used to fabricate diodes and metal oxide semiconductor field-effect transistors (MOSFETs) at microwave frequencies, and to manufacture the lasers used to read optical discs such as compact discs (CDs) and digital versatile discs (DVDs).

Molecular beam epitaxy (MBE) is an atomic layer by atomic layer crystal growth technique, based on reaction of molecular or atomic beams with a heated crystalline substrate, performed in an ultra-high vacuum (UHV) environment. The term molecular beam epitaxy was used for the first time in 1970. The term molecular beam describes a unidirectional kinematic flow of atoms or molecules with no collisions among them, as opposed to a viscous, fluid-like flow. The term epitaxy is composed of the Greek words epi meaning akin or upon, and taxis meaning arrangement or order. Epitaxy refers to ordered growth of one crystalline layer on another crystalline layer, with the same (or related) crystal arrangement. Therefore, a critical issue in epitaxial crystal growth is the surface conditions of the starting crystal (the substrate) and the subsequent layers as they are being grown.Molecular beam epitaxy is unique in two respects: it is performed in UHV, and it is based on the reaction of atomic and/or molecular beams with a crystalline surface, relying on kinetic processes such as adsorption, desorption, dissociation, migration, reaction, and incorporation. These features allow real-time, in situ monitoring and control during the substrate preparation and film growth, to ensure the best conditions for stoichiometry and epitaxy. Consequently, although MBE is a form of vacuum evaporation technique, it distinguishes itself from other evaporation crystal-growth methods by employing atomic or molecular beams in a UHV environment, which allows precise control of composition, growth condition, high purity, and real-time, in situ monitoring. Since the growth is governed by surface kinetics at relatively low substrate temperatures, material and dopant inter-diffusion can be kept to a minimum. Therefore MBE is capable of producing extremely high purity and highly crystalline thin-film heterostructures with precise control over composition, doping, and interfaces in the fraction of nanometer range in the growth direction, with precise lateral uniformity. The sub-nanometer control and precision in the structure and doping afforded by MBE, its variants, and MOCVD leads to an enormous flexibility in tailoring functional behavior of thin-film structures. This is referred to as band gap engineering or band structure engineering. Figure 1 shows the schematic geometry of MBE and deposition, and the key features leading to band gap engineering using MBE.

10.1 Molecular Beam Epitaxy (MBE)

Epitaxy is a form of crystal growth that relies on the underlying substrate to form a template for the continued material deposition, which enables the growth of structures that remain in a uniform crystalline state for optimal electrical and optical properties.

Molecular beam epitaxy (MBE) is an experimental technique utilized for layer-by-layer growth of thin films of various quantum materials. Out of the variety of thin film growth techniques available, MBE is considered to be one of the cleanest, but also one of the most technically challenging and demanding, as MBE growth takes place in ultra-high vacuum (UHV) environment.

Typical MBE experimental setup consists of two or more Knudsen effusion cells (K-cells), located at the left hand side of a ultra-high vacuum (UHV) chamber and aligned towards the center of the chamber where a sample holder with a substrate is located (Figure 21). Each individual K-cell contains a different element in ultra pure solid form (i.e. elemental 99.999% Selinum, Bismuth, etc.) which can be used in the thin film synthesis. The process of MBE growth starts by heating the K-cells to appropriate temperatures until the elements in each cell reach a sublimation point. Then, the shutters are opened and physical vapor from each K-cell diffuses though the chamber until it reaches the substrate where it gets deposited, and the thin film gets formed. The final composition and stoichiometry of the film will depend on the temperature and surface atomic structure of the substrate, as well as the flux ratios of individual components reaching the substrate. For more uniform growth, substrate can be continuously rotated at low rotation speeds (~ 1−2 rotations per minute) by utilizing a stepper motor attached to the magnetic manipulator.

To characterize the samples in-situ during growth, we use reflection high-energy electron diffraction (RHEED). Electrons emitted from the RHEED gun (Figure 1) incident at a very low angle with respect to the sample surface are diffracted, and the resulting diffraction pattern is observed on the screen. This pattern can reveal: (1) quality of the film surface, and (2) film thickness down to a single monolayer.

One reason that MBE is such a precise way of making a crystal is that it happens in highly controlled conditions: extreme cleanliness and what's called an ultra-high vacuum (UHV), so no dirt particles or unwanted gas molecules can interfere with or contaminate the crystal growth. "Extreme cleanliness" means even cleaner than the conditions used in normal semiconductor manufacture; an "ultra-high vacuum" means the pressure is so low that it's at the limit of what's easily measurable.

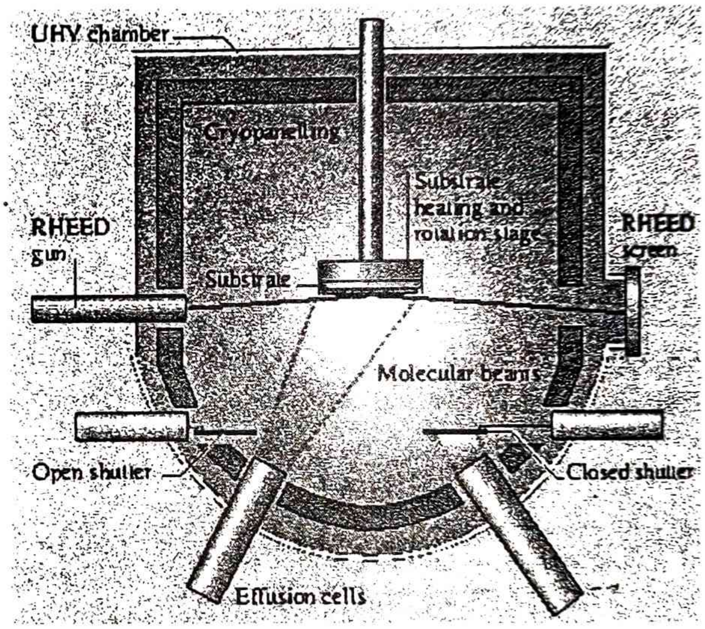

Figure 21: Schematic diagram of molecular beam epitaxy method.

10.2 Characteristics of MBE Growth

These are the characteristics of thin film or multilayer growth of materials using molecular beam epitaxy.

1. Low growth rate of ~ 1 monolayer (lattice plane) per sec.

2. Low growth temperature (~ 550^oC for GaAs).
3. Smooth growth surface with steps of atomic height and large flat terraces.
4. Precise control of surface composition and morphology.
5. Abrupt variation of chemical composition at interfaces.
6. In-situ control of crystal growth at the atomic level.

Examples: Molecular beam epitaxy is used to grow a wide range of materials. These materials include semiconductors, superconductors, metals, oxides, nitrides, and organic films. In almost all fields of nanotechnology, there is a drive to produce structures with ever smaller dimensions. Such structures are high performance devices with quantum confinement and some examples of these structures are IIIV semiconductors, GaAs/AlGaAs superlattice, quantum wells (QW s), quantum wires and quantum dots. Such low-dimensional structures form the basis of the quantum well lasers and pseudomorphic high electron mobility transistors (p-HEMTs) produced in huge volumes by MBE for optoelectronic and microwave applications. The combination of precise growth control and in-situ analysis makes MBE the prominent technology to meet such demands.

Some examples of MBE grown sophisticated lattice-matched heterostructures are: (Al,Ga)As /GaAs heterostructures, and layer sequence in quantum/cascade lasers (QCL). These heteroepitaxy materials may have dissimilarity in lattice parameter, crystal structure, bonding character, properties. Other examples are MnAs on GaAS, and GaN on LiO_2.

10.3 Advantage of MBE Growth of Quantum Dots

The advantages of using MBE for epitaxy over alternative methods of semiconductor growth include:

1. Low, controllable growth rate enabling compositional or dopant changes to be made on a sub-nanometre scale.
2. Compared with CVD, MOVPE etc., growth temperature is low ($\leq 650^oC$ for GaAs).
3. The Ultra-High Vacuum (UHV) environment allows diagnostic techniques to be performed in-situ, such as surface analysis by RHEED.
4. Sequential deposition can also be done in-situ.
5. Ultra-high purity material growth can be achieved.

6. Provision of source material is independent of substrate temperature, as opposed to MOVPE where the substrate temperature influences metal-organic compound cracking. This allows for a much wider substrate temperature operating range.

10.4 Disadvantage of MBE Growth of Quantum Dots

In spite of several advantages of the MBE growth process, it suffers from several disadvantages as well. These disadvantages are listed below:

1. It is a very complicated process.
2. For overall perfect and pure film, it is necessary to maintain a very low pressure of the order of 10^{-10} Torr, which is really a challenging task.
3. This process is very expensive as compared to the process like chemical vapor deposition.
4. The growth rate in MBE process is 0.01 0.3 gm/min which is very small compared to the growth rate of 1 m/min in CVD process.